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The stereospecific hydrogenation and dehydrogenation of rosin and fatty acids

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THE STEREOSPECIFIC HYDROGENATION AND DEHYDROGENATION OF ROSIN AND FATTY ACIDS

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ABSTRACT

Tall oil is a byproduct of the standard wood pulping process in the paper industry. It is primarily made up of C:18 fatty acids, rosin acids and a minor fraction of neutrals. Normally, tall oil is further distilled into fractions and then hydrogenated or dehydrogenated into different products. In this project, three heterogeneous catalytic methods of producing byproducts of various distilled tall oil fractions were examined at lower temperatures and pressures than the industry norm in an attempt to develop cheaper production processes. Reactions were conducted in stirred batch reactors of different sizes and product compositions were analyzed primarily by GC/MS and GC.

The selective hydrogenation of abietic acid, a common rosin acid, to abietyl alcohol in the presence of fatty acids was examined first. For the conditions and catalysts used, the yield to abietyl alcohol was small and the reaction was not selective, giving both ring hydrogenation and dehydrogenation.

Second, the dehydrogenation of abietic acid to dehydroabietic acid in a primarily rosin feed was studied. The Pd/C class of catalysts had the greatest activity. There was a maximum yield of 58% associated with equilibrium, and the reaction took place predominantly as a disproportionation. The reaction was very slow at temperatures less than 230^{o}C, and decarboxylation occurred in greater abundance as time or temperature of the reaction was increased. In the mainly rosin feed (HYR), some polymerization occurred; however, the amount of polymer was relatively small, the polymer was thermally labile and most likely thermal in origin. Finally, the gas environment (H_2, N_2, air) did not have a significant effect on the reaction.

The final reaction studied was the selective hydrogenation of unsaturated fatty acids to unsaturated fatty alcohols in a mainly fatty acid feed. The results showed that the hydrogenation could not occur to a significant degree at conditions less than 250^{o}C and 87 bar, for any of the common classes of hydrogenation catalysts.

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction and Goals

The purpose of this project is to study the catalytic hydrogenation and dehydrogenation of two pine resin fractions – (a) distilled tall oil (DTO); (b) fatty acids. Tall Oil is a byproduct of the pulping process in the forestry industry. Tall Oil is made up of three main components with varying concentrations normally associated with the type of tree: fatty acids, rosin and a certain amount of neutrals considered impurities. Normally Tall Oil is distilled into different fractions in order to increase value, hence DTO.(Norlin, 2000) The fatty acids associated with tall oil are mainly C18 straight chains with carboxylic acids on one end and, depending upon the fatty acid, differing numbers of double bonds. Figure 1.1 shows linoleic acid; the Z's denote either cis or trans.

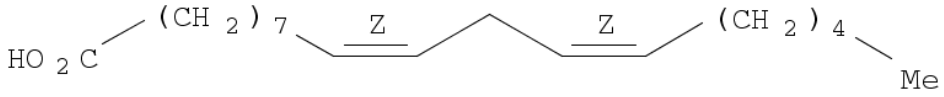

Figure 1.1 Linoleic Acid

Oleic acid is the same as linoleic, except one less double bond, and stearic acid has no double bonds. Rosin consists mainly of tricyclic acid compounds, most of which are terpenes. Abietic Acid is the primary rosin acid found in tall oil and is pictured below in Figure 1.2. There are many isomers of abietic acid depending on the placement of the double bonds within the structure. Pimaric acid is another common rosin acid which is shown in Figure 1.2. (Fiebach, 2000)

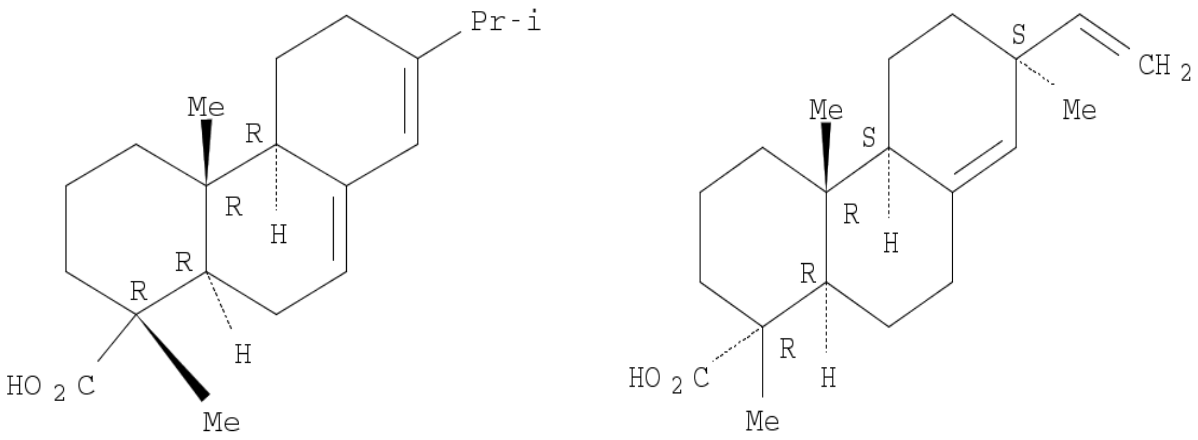

Figure 1.2 Abietic Acid (Left) and Pimaric Acid (Right) structures

For this purpose I used typical heterogeneous hydrogenation and dehydrogenation catalysts, which are usually based on group VIIIB or VIB transition metals supported on activated carbons, alumina, silica, etc. The behavior of such reduced metals can vary significantly with support (especially acidity/basicity and hydrophobicity/hydrophilicity) and environment, in this case, the H_2 partial pressure and whatever amounts of water and sulfur are present. Three different catalytic reactions were studied: (1) the hydrogenation of abietic acid to abietyl alcohol in the presence of fatty acids, which is desired to occur along with minimal conversion of the fatty acids; (2) the dehydrogenation of abietic acid to dehydroabietic acid; (3) the hydrogenation of a primarily fatty acid product stream to fatty alcohols, with the goal being to limit the hydrogenation of C=C bonds. The structures of desired products abietyl alcohol, dehydroabietic acid and oleyl alcohol are shown below in Figures 1.3. The ultimate aim of the project was to determine the feasibility of catalytically converting different industrial pine resin product streams into more diverse, useful and economically viable chemicals. Rosin alcohols are often used as plasticizers and adhesives, while rosins that are disproportionated can be used as emulsifiers in polymerization processes and are much less susceptible to oxidation. (Fiebach,

2000) Fatty Alcohols are used as raw materials in the production of cosmetics, pharmaceuticals, and liquid detergents. (Sanchez, 2011)

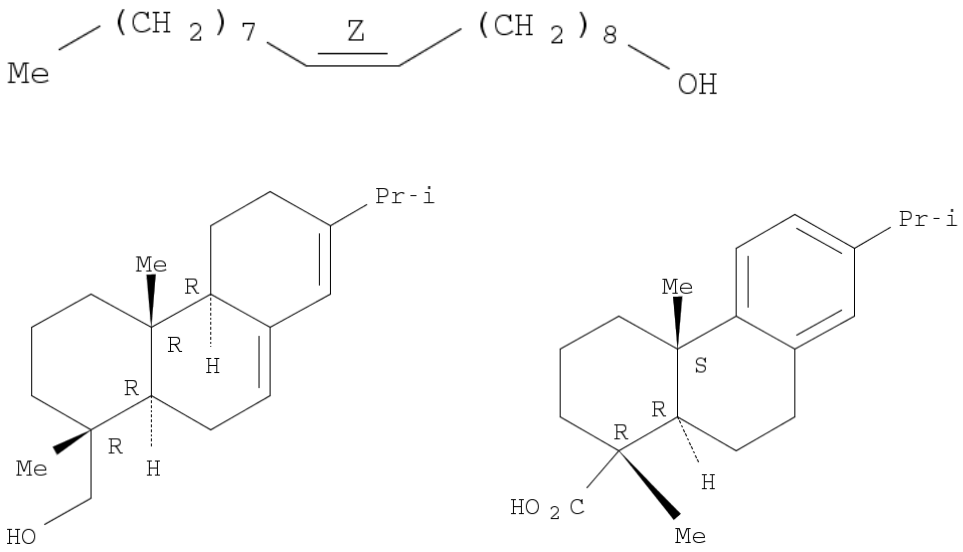

Figure 1.3 Oleyl Alcohol (Top), Abietyl Alcohol (Bottom Left), and Dehydroabietic Acid (Bottom Right)

1.1.1 Literature Review: Hydrogenation of Abietic Acid to Abietyl Alcohol

Abietyl alcohol (CAS 666-84-2; formula $C_{20}H_{32}O$; MW = 288.47) is the alcohol of abietic acid. Because a typical DTO also contains fatty acids, and because the ring hydrogenation products of abietic acid are less stable, it is desired to hydrogenate at the carbonyl position only to make abietyl alcohol. A literature search revealed that this reaction may be selective in the homogeneous phase at ambient temperature with $LiAlH_4$ reductant, and also to a lesser extent with $NaBH_4$. (Brown and Rapoport, 1963; Molaison et al., 1959; Jagdale and Sudalai, 2008; Burstahler and Marx, 1967) The reduction of carboxylate esters to alcohols with an equal molar ratio of $NaBH_4$ to ethanedithiol to ester was accomplished with approximately 80% yields at room temperature (Guida et al., 1984). Abietic acid can also be reduced

selectively at 130ºC with sodium ethoxide in excess ethanol (Hansley, 1947). Heterogeneous catalysts reported to give a high conversion include a supported Ru-Sn bimetallic in 2/1 diglyme on alumina at 260ºC with an 84% yield to rosin alcohol (Tahara et al., 1996), and Cu_2CrO_4 (Adkins' Catalyst) at 300ºC (Mugishima et al., 1957, in both cases at 100 atm H_2 pressure (1500 psig). None of this work was carried out in the presence of fatty acids, and there was no other heterogeneous work at low temperature which selectively produced the alcohol, although there were several papers where dihydroabietic acids were produced. Lombard et al. (1953) reported that Raney Ni, PtO_2, and Pd-C to be three catalysts capable of producing dihydroabietic acid.

1.1.2 Literature Review: Dehydrogenation of Abietic Acid

A pine resin DTO can also be dehydrogenated at ~200-330C, with the primary reactions the dehydrogenations of the rosin acids, e.g., abietic acid to dehydroabietic acid. We found no literature results for the catalytic dehydrogenation of rosin acids in the absence of large amounts of either fatty acids (Floyd, 1952; McBride and Wheelus, 1968) or pimaric/isopimaric acids (Song et al., 1985; Wang et al., 2009). Table 1.1 gives details of these literature data. The weight ratio is the weight of feed per weight of catalyst. The products are mostly dehydroabietic acids and phenanthrene carboxylic acid derivatives of abietic, pimaric and isopimaric acids, although other dehydrogenation products are probably present.

Table 1.1 Dehydrogenation Tests, Inert Gas, from Literature

Cat.	Wt. Ratio	Feed Comp.	Time, h	T, °C	% Conv.
Ni/SiO_2[1]	20	72% rosin, 24% fatty acids	2	250	100
Raney Ni[1]	20	36% rosin, 61% fatty acids	3	250	100
Poly (thioresorcinol)[2]	10-50	13% rosin	3-6	290-320	100
5% Pd/C[3]	1000	93% rosin, 4% fatty acids	2	270	100
5% Pd/C[4]	50	W.V. gum rosin	3.5	210	58
5% Pd/C[5]	1000	Guangxi Wuzhou gum rosin	2	220	42
5% Pd/C[5]	1000	" "	2	250	62

1. Floyd, 1952.
2. McBride and Wheelus, 1968.
3. Song et al., 1985; the rosin acids included 22% pimaric/isopimaric acids.
4. Loeblich and Lawrence, 1956; the feed was not characterized, but a gum rosin of this type typically contains >20% pimaric/isopimaric/communic acids (Soltes and Zinkel, 1989).
5. Wang et al., 2009; the rosin included >10% pimaric/isopimaric acids.

1.1.3 Literature Review: Hydrogenation of Fatty Acids

The final reaction of a DTO feed that was examined was the hydrogenation of a mixed fatty acid feed to fatty alcohols. This feed is comprised primarily of C18 fatty acids, linoleic, oleic and stearic. The linoleyl alcohol hydrogenation product is normally preferred, but a mixture of linoleyl (two double bonds) and oleyl (one double bond) is considered acceptable.

The literature in the area of catalytic hydrogenation of carboxylic acids and esters to alcohols is fairly extensive, but the range of industrial catalysts used to date is relatively narrow – mostly Fe-, Zn-, or Cu-based. Many processes start with esterified feedstock, often esterified

with methanol (FAMEs), to limit corrosion and prevent the formation of salts from the active catalytic metal. The metal salts, once formed, can leach from the catalyst.

Typical catalysts for FAME feeds are supported (usually on SiO_2) Cu/Cr and Cu/Zn operated at 190-220ºC to obtain a more saturated product and <150ºC for a slightly less saturated one (Pelzer et al., 2004). The rates are low: even at 270 atm of H_2, a Cognis patent application quotes a liquid hourly space velocity [liquid volume/(cat. volume * time)] of only 1.5 h^{-1} for a continuous reactor (Pelzer et al., 2004). Most of the other Cu-based catalysts are also operated around 240-280 atm (near 4000 psi, Corma et al., 2007). The products are highly saturated.

Corma and co-workers (2007) recently reviewed the entire field and concluded that Cu-based catalysts cannot give adequate selectivity to unsaturated fatty alcohols. While Zn/Al_2O_3 and Fe/ZnO catalysts can, they require pressures above 200 atm if a solvent is not used. Corma suggests that the future for selective hydrogenation at the carbonyl position is in Ru-based alloys. There is a large amount of recent work on these for other types of catalytic hydrogenations, along with Co-, Pd-, Pt- and Rh-based alloys. The typical alloying materials are Sn, Zn and B – Sn and B with Ru and Co, Sn and Zn with Pt and Pd. There has been work on Ru/Sn/B and Co/Sn/B alloys for hydrogenating fatty acids. In initial work with FAMEs, Deshpande et al. (1990) found 91% selectivity to alcohol at 99% conversion for $Ru\text{-}Sn/B_2O_3$ and Narasimhan et al. (1989) found 89% selectivity at 68% conversion for $Ru/Sn/\alpha\text{-}Al_2O_3$ (both at 270ºC, 45 bar, 40/1 substrate/catalyst). Toba et al. (1999) obtained ~70% selectivity at 100% conversion with $Ru/Sn/Al_2O_3$ at 240ºC and 65 bar. But all of these used saturated fatty acid (mostly stearic acid) feeds, so there was less of a selectivity issue.

There are some other new approaches to the selective hydrogenation of acids to alcohols. Propane has been used as a supercritical fluid to increase the H_2 solubility by generating a single

phase. At 280ºC and ~150 atm a group was able to convert 90% of a FAME feed at high space velocity (LHSV ~2400 h^{-1}) with a $Cu/Fe/SiO_2$ catalyst, but 75 mol% propane (20 mol% H_2) was necessary, and the product was heavily saturated (van den Hark and Harrod, 2001). It is also claimed that Pd-based catalysts can hydrogenate selectively at the carbonyl, when used as Pd(IV) homogeneous complexes with phosphite ligands (Liu et al., 2010), at 70 atm and 200ºC. However, the substrate/catalyst ratio was very low, and the reactions were performed in toluene/water solvent. It was concluded that there are no examples of selective (at the carbonyl position) catalytic hydrogenation of an unsaturated fatty acid feed except at high pressures or in the presence of large amounts of solvent.

CHAPTER 2: EXPERIMENTAL PROCEDURES

2.1 Hydrogenation of Abietic Acid

The following describes experimental procedures for hydrogenation reactions of a mixture of rosin and fatty acids, and denoted as a distilled tall oil (DTO). The goal is to hydrogenate as much of the abietic acid as possible to abietyl alcohol. There will also be hydrogenation of the fatty acids.

2.1.1 Feed Composition

The synthetic DTO/fatty acid feed was prepared at Arizona Chemical and shipped to LSU. It was prepared from commercial linoleic and abietic acid (both Acros, technical grades) in a 72/28 ratio (by weight). The feed composition (wt%) as analyzed by GC at Arizona Chemical is shown in Table 2.1.

Table 2.1 Composition of Synthetic DTO (AZ-1)[1]

STEARIC ACID - (C18:0)	0.26
C18:2 ACID ISOMERS	0.10
LINOLEIC ACID (c9,c12)	70.72
CONJ. LINOLEIC ACIDS (18:2)	0.57
PIMARIC and/or 8,15-PIMARIC ACID	0.18
SANDARACOPIMARIC ACID	0.08
UNKNOWN ROSIN ACID PEAK(S)	0.12
PALUSTRIC ACID	1.04
ISOPIMARIC ACID	0.27
NON-CONJ. ABIETIC ACIDS PEAK(S)	0.25
ABIETIC ACID	24.41
DEHYDROABIETIC ACID	1.40
NEOABIETIC ACID	0.12
POLYUNSATURATED ROSIN ACIDS	0.16
UNKNOWN ROSIN ACIDS/UNKNOWNS	0.32
TOTAL WEIGHT PERCENT BY GC	100.00

[1]Analysis provided by Dr. Donald Scott of Arizona Chemical. The designation 18:2 means an 18 carbon chain with two internal C=C bonds.

2.1.2 Reaction Procedure

Bomb reactors of ~20 mL volume fabricated from 3/4" Swagelok VCR fittings and stainless steel tubing stock were used. The upper VCR fitting was tapped with 1/8" F-NPT and fitted with a 1/8" Swagelok angle valve to allow gas to enter. The reactors (usually four at a time) are housed in an aluminum heating block which is heated by four cartridge heaters. During reaction, the heating block was rotated by a cam/motor at ~1 Hz; in this way the contents of the reactors were kept mixed.

The reactors were first filled with catalyst, and then purged with N_2 (UHP) for three fill/release cycles. Then the reactors were filled to 100 psig H_2 (industrial grade, at 150 psig if a 40% H_2/N_2 mixture was used), for two fill/release cycles, then filled again to 100 psig for catalyst reduction. Reduction was for ~30 min at an appropriate temperature for the catalysts used. This was for catalyst cleaning purposes only, as all catalysts had been previously reduced in quartz calcining tubes prior to their use here. After reduction/cleaning the temperature was reduced, the reactors were vented to slightly above atmospheric pressure, the heated liquid feed added by syringe through the valve (covered by a rubber septum), and the reactors filled to the initial reaction pressure, at ambient temperature. The initial pressure is what is quoted in the tabular results. This pressure can be maintained at this value by keeping the valves opened to the reactors; in this way there was always enough H_2 provided. This was not done for run series 1-3, for a variety of reasons (mainly worries about leaks and vapor pressure), and so these early runs may have been H_2-limited.

2.1.3 Sample Analysis

After the reaction, the reactors were cooled, vented slowly and opened. The contents, which were either solid or liquid (no two phase samples), were split into two portions. One portion was dissolved at roughly 100 mM (calculated on a feed basis) in deuterated chloroform for NMR analysis. The other portion was dissolved in equal volumes of methanol and diethyl ether, then titrated with 15% TMAH solution (in spec grade methanol) to a pink endpoint, and analyzed according to a standard procedure (Arizona Chemical, 2008) in an HP-5890 GC with a MS (HP-5972) detector. The titration was a derivatization designed to convert most or all of the acids to methyl esters and the alcohols to methyl ethers. The column was the same as described in this method (Supelco SP-2380, 30 m long, 0.25 mm id, 0.20 micron film thickness), but the temperature program was slowed down to 50-60 min total time with a final temperature of 230°C. This was done (after some trial and error), in order to improve the separation of the esters (acids) from the ethers (alcohols). The initial oven temperature (150ºC) and initial time (5 min) were retained. Further details on the chromatography are given in Appendix A.

The NMR results were obtained on a 400 MHz Bruker instrument, both ^{1}H and ^{13}C analyses. These were used primarily for confirmation of the GC-MS results, especially to search for alcohol formation. It is easier to identify the fatty and rosin alcohols by NMR, and the NMR results prompted us to improve our GC-MS methods to better separate the alcohols. Unfortunately, it is very difficult to distinguish linoleyl and oleyl alcohols by NMR, but one can determine an aggregate amount.

2.2 Dehydrogenation of Abietic Acid

The following is the experimental procedure for the dehydrogenation of abietic acids to dehydroabietic acids in a mainly rosin acid feed.

2.2.1 Feed Composition and Catalyst Characterization

The DTO feed was Arizona Chemical Sylvaros HYR, lot #B05012121. The feed composition (wt%) was reported by Arizona Chemical as 93.8% rosin acids, 2.7% fatty acids, and 2.1% unsaponifiables (Arizona Chemical, 2007). The gum rosin feed (TAO, CAS 8050-09-7) was from Sciencelab.com Inc., #SLR1003 and contains 99% rosin acids and 1% unsaponifiables.

The contact pH of a catalyst was measured by suspending 1 g catalyst in 10 mL DI water until the pH stabilized (~30 min). The dispersion of the active metals in the catalysts (% of active metal atoms actually exposed on a surface) were measured by pulsed CO or H_2 adsorption at 25ºC, using a Micromeritics 2700 Pulsed Chemisorption unit. The standard assumption of 1 mol H-atoms/mol Pd or Pt was made. A dispersion of 100% means that the all Pd or Pt atoms are accessible for adsorption. The dispersions for Pd supported on activated carbon catalysts were measured using pulsed CO adsorption at 25ºC, which is considered more accurate for carbons than H_2 adsorption. The supported Ru dispersions were also determined by pulsed CO adsorption. The standard assumption of 1 mol CO/mol Pd or Ru was made. The chemisorption results are tabulated in Table 3.1.

2.2.2 Reaction Procedure

Two stirred autoclaves (500 mL and 1 L volumes) were used for the reactions at elevated pressures, and 250 mL glass reactors (with stirbars) for the reactions at atmospheric pressure. The autoclaves were always in contact with the N_2 (UHP) gas supplied by a cylinder, while the glass reactors were continuously fed N_2 gas that exited through the top of a water condenser to a bubbler of mineral oil. All temperatures were controlled to within 3ºC once the final temperature was reached, except where noted in Appendix B. For the autoclaves, the catalyst was contained within a spinning basket on the shaft; for the glass reactors, it was stirred along with the liquid. It takes both the autoclaves and the glass reactors about 0.5-1 h to cool to the melt temperature after the heat is cut off. This is why a "post reaction" sample of the final solid was analyzed in many of the runs below. Two runs were also performed with the 500 mL autoclave vessel exposed to air, within a drying oven, with no catalyst. The mass recoveries from the reactors were 94-96%, and this does not count the samples withdrawn during reaction.

2.2.3 Sample Analysis

Samples were taken through sample valves (autoclaves) or with pipets (glass reactors) through one of the reactor ports, while raising the flow of gas. The samples, which were all solid at room temperature, were analyzed by GC-MS as in Section 2.1.3. The same samples were also analyzed for dimer and other oligomers by a high temperature GC (HTGC) method (Arizona Chemical, 2003), using the same column, temperature program and response factors as specified in this method. The column was a 6QC5/HT5 polyamide clad capillary column, 6m , 0.53mm I.D., 0.1µm film. The temperature program had an initial temperature of 40°C with a ramp rate

of 10°C per minute to 160°C with a 10 minute hold and then a 15°C ramp to 380°C with a final hold of 20 minutes.

The GC-MS results are reported without any correction made for numbers of electrons – for an EI-MS, the response is roughly proportional to electron number. The correction is unnecessary since the electron counts and molecular weights for all the compounds fall within a very narrow range So the raw area%'s may be taken as characteristic of both mol%'s and wt%'s.

2.3 Selective Hydrogenation of Fatty Acids to Fatty Alcohols

The following is the experimental procedure for the hydrogenation of fatty acids to fatty alcohols, with a mainly fatty acid feed.

2.3.1 Feed and Catalyst Characterization

The FA-1 feed was supplied by Arizona Chemical to LSU. A typical analysis (there is some variation) per Arizona Chemical is (wt%): unsaponifiables, 2.2; rosin acids, 0.8; fatty acids, balance. Of the fatty acids, the breakdown is typically (wt%): stearic, 2; oleic, 50; non-conjugated linoleic, 37; conjugated linoleic, 7; other fatty acids, 4. The acid value is ~196 mg KOH/g, the Wijs Iodine value 130, the specific gravity 0.898, the viscosity 20 cp, and the flash point 204ºC. The catalyst characterizations were preformed exactly as described in section 2.2.1.

2.3.2 Reaction Procedures

The bomb reactors described in section 2.1.2 were used again, along with a mini-autoclave of ~30 mL capacity that was used for one run, with the same procedure. The reactors

were first filled with catalyst, and then purged with N_2 for two fill/release cycles. Then the reactors were filled with H_2 and heated to the appropriate temperature. The pressure was maintained at the stated value by keeping the valves opened to the reactors; in this way there was always enough H_2 provided.

2.3.3 Sample Analysis

After the reaction, the reactors were cooled, vented slowly and opened. The contents, typically solid at room temperature unless diluted with methanol, were split into two portions. One portion was titrated/derivatized as stated in Section 2.1.3The GC-MS analysis was also similar, but the temperature program was altered to obtain better peak separations. The program for the FA-1 feed and products was: 120ºC, 1 min, 2ºC/min to 130ºC, 1ºC/min to 140ºC, 4ºC/min to 220ºC, 12 min final hold. Some of the same samples were also analyzed for polymer by the Arizona Chemical HTGC method as stated in Section 2.2.3., using the same column, temperature program and response factors as specified in this method, however in these cases the amount of polymer found was negligible.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 Compound Identifications by GCMS

Compound identifications in MS were made both by analysis of the EI fragment patterns and by injections of standards (stearic, oleic and linoleic acids, abietic acid, stearyl and oleyl alcohols). In this manner it was determined that the esterification procedure etherifies some (but not all) of each alcohol. Therefore any single alcohol can appear at two different elution times, for the alcohol and its ether. Standards for the rosin alcohols could not be located, and so the identification of dihydroabietyl alcohol was made on the basis of fragment analysis only (m/e of the etherified alcohol at 275, 259, 243, 215) and its position in the chromatogram with the fatty alcohols, after linoleic acid and prior to abietic acid. The 275 peak corresponds to a loss of 2 methyl groups, while 259 represents the loss of the entire ether chain. The 243 peak is associated with the loss of another methyl group in addition to the ether chain and 215 corresponds to the loss of the ether chain and the propyl group. The dihydroabietic acids appear in this region also, thus the reason for the very long analysis times to obtain adequate peak separation. The etherified alcohol has a parent m/e of 304 and this fragment was not observed. Abietyl alcohol was also not observed by GC-MS, but there was a small NMR peak at 3.3-3.4 ppm suggesting some may have been present.

The GC-MS results are reported without any correction made for numbers of electrons – for an EI-MS, the response is proportional to electron number. The correction is unnecessary since the electron counts for all the compounds fall within a narrow range – e.g., 150 electrons for linoleyl alcohol to 168 for dihydroabietic acid. The number of electrons for each component was used to correct the results from a single run, and it was determined that the computed

mol%'s differed from area%'s by <5%, within detector error. So the area%'s reported here may be taken as characteristic of mol%'s.

It is very difficult to separate and identify oleyl and linoleyl alcohols by GC-MS. First, both have weak parent and m-1 ions. The ion at m/e = 281 (m-1) is characteristic for etherified oleyl alcohol and was sometimes present in enough quantity to enable identification on this basis. But a single characteristic ion for the non-etherified oleyl alcohol could not be located. In the results below the oleyl and linoleyl alcohols are grouped together. All positional isomers are also grouped together, so (e.g.) abietic acid would include palustric, pimaric, etc. Representative chromatograms can be found in Appendix A.

3.2 Catalysts and Their Sources

The catalysts were derived from both industrial suppliers and by synthesis. Synthesis was necessary for the Pd, Ru, and Pt alloy catalysts; these are specialty materials and are not generally available from the standard suppliers. The SiO_2-supported catalyst (Pd_S2) is easy to make in high dispersion (e.g., Reagan et al., 1981). Almost all the Pd or Pt catalysts used here were already tested for H_2 dispersion (dispersion = mols H-atoms adsorbed*100/mol Pd or Pt in catalyst), to determine how much Pd or Pt was on the surface, and whether the adsorption of H_2 was in the range normally associated with the alloy. Typical commercial Pd and Pt catalysts on most supports show >60% dispersions at low loadings and ~20% at high (e.g., 5 wt%) loadings. When supported on SiO_2, dispersions can be higher. Alloying of Pd or Pt with Cu, Sn and Zn leads to lower dispersion, but often higher selectivity for carboxylate vs. C=C double bond hydrogenation. The catalysts used and their dispersions (where measured) are shown in Table 3.1. The low dispersion (large metal particle size) Pd/Cu catalyst was made that way

deliberately (Bussard, pp. 66-67); because it is thought that larger metal particle sizes are more selective for carboxylate hydrogenation.

The major differences between Pd/C "D", "E" and "M" are: (a) the "D" carbon is slightly less basic than "E"; (b) the "D" carbon is of the "eggshell" type, i.e., its active sites are concentrated near the external particle surface rather than uniformly distributed throughout the particle; (c) "D" is more pyrophoric and so is supplied in a wetter state (this is why the feed/catalyst weight ratios for "D" were kept lower – to account for the water present in the catalyst); (d) the "M" is an almost neutral carbon. Since "B" and "E" are from the same supplier, they probably have similar surface properties, as seen by the contact pH of the catalysts. For the hydrogenations to rosin alcohols, at least one catalyst of every type thought to be selective for carboxylate hydrogenation was used, based on the catalysis literature for the last 30 years.

Table 3.1 Catalysts Used

Name	Source	Composition, wt%	Contact pH	Disp., %
Pd/C E	Engelhard (BASF)	5% Pd/activated carbon	9.3[1]	35[1]
Pd/C D	Degussa	5% Pd/activated carbon	8.2[1]	18
Pd/C M	Sud-Chemie	5% Pd/activated carbon	7.0[1]	36
Pd/C B	BASF	2% Pd/activated carbon	9.8	38
PdAl3	Engelhard (BASF)	0.5% Pd/Al_2O_3		69
Pd_S2	Synthesis	3% Pd/SiO_2		89
PdSn1	Synthesis[3]	1% Pd/0.5% Sn/Al_2O_3		
PdCu2Al	Synthesis[3]	1% Pd/0.5% Cu/Al_2O_3		19[2]
PdCu3Al	Synthesis[3]	1% Pd/1% Cu/ Al_2O_3		67[2]
PdCu4Al1	Synthesis[3]	1% Pd/0.5% Cu/ Al_2O_3		50[2]
PtAl1	Johnson Matthey	0.5% Pt/ Al_2O_3		75[2]
Pt_S2	Synthesis	3% Pt/SiO_2		50
I-26	Synthesis	1% Pt/0.5% K/76% ZnO/ Al_2O_3		

(Table 3.1 continued)

I-27	Synthesis	1% Pt/1% ZnO/Al_2O_3	
I-28	Synthesis	3% Ru/5%Sn/B/TiO_2	3.5, 7.3[5]
I-29	Synthesis	3% Ru/7%Sn/TiO_2	4.1, 1.3[5]
Ru/HAP-3	Synthesis	13% Ru/hydroxyapatite	
I-25	Synthesis	75% Co/25% B	
CoSi1	Synthesis[4]	8% Co/aminated SiO_2	
NiSi1	Grace-Davison	60% Ni/SiO_2	
Raney Ni	Grace-Davison	59% Ni/Al	
CuCr	Johnson Matthey	2 CuO•Cr_2O_3	
	Sud-Chemie		
G22/2	BASF	47% CuO, 34% Cr_2O_3,	
		6% BaO, 13%SiO_2	
Cu-1986T		69%Cr_2CuO_4,	
		19% CuO,5% MnO_2,	
		3% Na_2SiO_3,binder	

[1]Liu, pp.25-26
[2]Bussard, p. 68
[3]Bussard, p. 61-63
[4]Song, pp. 23-25
[5]The first number was measured after reduction at 250^{o}C, and the second after reduction at 400^{o}C.

Many of these catalysts were made for use in three previous projects, thus the diverse nomenclature. All those synthesized for previous projects are known to be active hydrogenation catalysts, and were prepared using common catalytic alumina, silica and hydroxyapatite supports. The only catalysts specifically synthesized for this project are listed below.

I-25 – 75%Co/25%B (wt%) alloy was made by sodium borohydride (3.0 M solution, 7.3 mL, added dropwise) reduction of a cobalt acetate solution at ambient temperature. The acetate solution consisted of 45 mL ethanol, 20 mL water, 2.0 g of cetyltrimethylammonium bromide, 3.0 g of $Co(CH_3COO)_2$, and 1 mL of antifoaming agent (vegetable oil). The black solid was washed with water to near pH 7, followed by extraction in 25 mL of ethanol overnight at 80ºC, and extraction with another 25 mL under reflux for ~2 h. It was dried at 100ºC and calcined with N_2 for 2 h at 200ºC. The procedure was adapted from Liaw et al., 2008.

I-26 – 1%Pt/0.5%K/76%ZnO/Al_2O_3 (wt%) was made by incipient wetness impregnation (H_2PtCl_4) of a standard $K_2O/ZnO/Al_2O_3$ sol-gel porous oxide (calcined at 350ºC) with 1.5 mL solution/g catalyst, followed by drying at 100ºC and reduction at 400ºC with 20% H_2 for 6 h.

I-27 – 0.5%Pt/1%ZnO/Al_2O_3 was made by incipient wetness impregnation of $Zn(CH_3COO)_2$ onto commercial 0.5% Pt/Al_2O_3 (Aldrich) at 1.5 mL solution/ g catalyst followed by drying at 100ºC and reduction at 400ºC with 20% H_2 for 6 h.

I-28 – 3 wt%Ru with 4/1 Sn/Ru molar on TiO_2. Anatase TiO_2 (Alfa) was dried in air at 250ºC, then impregnated at incipient wetness with a solution of $RuCl_3 \bullet 3\ H_2O$ and tetrabutyltin in ethanol (~1/1 liquid volume per catalyst weight). It was left undisturbed for 12 h. Then $NaBH_4$ solution was added dropwise as reductant, 30/1 $NaBH_4$/Ru (~ 3 M), and the slurry stirred 15 min. Finally, the catalyst was filtered, washed with water until near neutral pH, washed 3 times with ethanol, and dried under flowing N_2 at 120ºC for 4 h and later reduced at 220ºC for 2 h. This procedure was adapted from Narasimhan et al., 1989, and Pouilloux et al., 1998.

I-29 – 3wt% Ru with 2/1 molar Sn/Ru ratio on TiO_2. Procedure same as above except: (a) no boron addition; (b) no washings; (c) after the inert gas treatment, it was oxidized with air

at 350ºC for 4 h, then switched to inert gas while cooling to 250ºC, then reduced with H_2 at 250ºC for 2 h. This procedure was adapted from: same as above, and also Silva et al., 2009.

Ru-HAP-3 – 13% Ru/hydroxyapatite (wt%). The hydroxyapatite support ($Ca_{10-n}(PO4)_{6-2n}(HPO_4)_{2n}(OH)_2$, n = 0.595) was prepared according to the procedure of Bett et al. (1967), with a surface area of 79 m^2/g. It was wet impregnated (20 mL/g catalyst) with a solution of $Ru(NH_4)_2Cl_5$, stirring at ambient temperature for a day. After filtration, it was washed with water, dried at 100ºC overnight, and reduced in H_2 for 2 h at 220ºC.

Pd_S2 and Pt_S2 – 3 wt% metal. To dry Davison Grade 57 silica, either $Pd(NO_3)_2 \bullet 2 H_2O$ or $Pt(NH_3)_4(NO_3)_2$ was impregnated from concentrated aqueous solution by incipient wetness. They were dried at 120ºC for 3 h, calcined in flowing air at 260ºC for 2 h, then flowing N_2 for 30 min, then switched to 20% H_2/N_2 and reduced at the same temperature for 2 h. The Pt catalyst was given an extra reduction treatment at 450ºC for 2 h.

3.3 Hydrogenation of Abietic Acid

A significant number of catalysts were screened in order to selectively hydrogenate abietic acid to abietyl alcohol in the presence of fatty acids. The kinetics data for the activities of these catalysts are reported in terms of % yields. Since there are two primary reactants (linoleic acid and abietic acid), yields can be defined based on both of them, in each case adding to 100%. Yield is just the product amount divided by the feed amount (time = 0), expressed as a percentage. Therefore the maximum yield if all abietic and all linoleic acids were converted to other products would be 200%. The products of abietic acid conversion include dihydroabietic acids, dihydroabietyl alcohol, and dehydroabietic acids. A summary of the GC/MS data for all runs, including yields, is given in the Appendix.

The feed used in these reactions is the one described in section 2.1.1. The ratio of rosin:fatty acids shown in Table 2.1 was confirmed at LSU by GC-MS. This mixture was in turn spiked with 75 ppmw dibenzothiophene and 75 ppmw of thioxanthene, to simulate the sulfur compounds and amounts in Arizona Chemical Sylvatal D30LR, a commercial DTO.

The identification of the exact sulfur impurities (~150 ppmw total per Arizona Chemical) was attempted for commercial Sylvatal D30LR, using both the GC-MS and a GC with a sulfur-specific detector (Varian 3800), but the GC-MS was not sensitive enough to identify them. While some small S-containing compounds could be seen using the GC with the S-specific detector, they could not be identified. From their location in the chromatograms they appeared to be rosin acid-type compounds containing sulfur, so typical aromatic compounds with a sulfur heteroatom were chosen to model the chemical behavior.

A reasonable comparison of the catalyst selectivities at high pressure conditions was obtained at baseline conditions of 170ºC, 250-500 psig H_2, 1-1.5 h reaction time, 20-40 ratio of feed volume/catalyst weight. This comparison is shown for the Pd-based catalysts in Figures 3.1a and 3.1b.

These results in Fig. 3.1 show that the PdSn1 catalyst is inactive; the others are all active for double bond hydrogenation of fatty acids, while the Degussa 5% Pd/C (Pd/C D) is also very active for the double bond hydrogenation of abietic acid. None of the Pd-based catalysts showed great promise for selective alcohols production, at these or any other conditions tried (120 or 200ºC, lower pressures). However, of the catalysts used the $Pd/Cu/Al_2O_3$ alloy catalysts were the most active for rosin alcohol production. With large reactants such as these it is likely that the reactions are diffusion-limited, so an eggshell catalyst such as Pd/C D should be more active than one where Pd is distributed evenly throughout the particle. Otherwise the catalysts appear

similar, and the Pd/C E catalyst did behave similarly to the "D" catalyst at 200ºC. At even higher temperatures and low pressure (250ºC, 40 psig H_2) dehydroabietic acid dominates the products from abietic acid (76% yield in 1 h at 10/1 reactant volume/catalyst weight ratio), but there was still very high conversion of linoleic to stearic and oleic acids (88% combined yield).

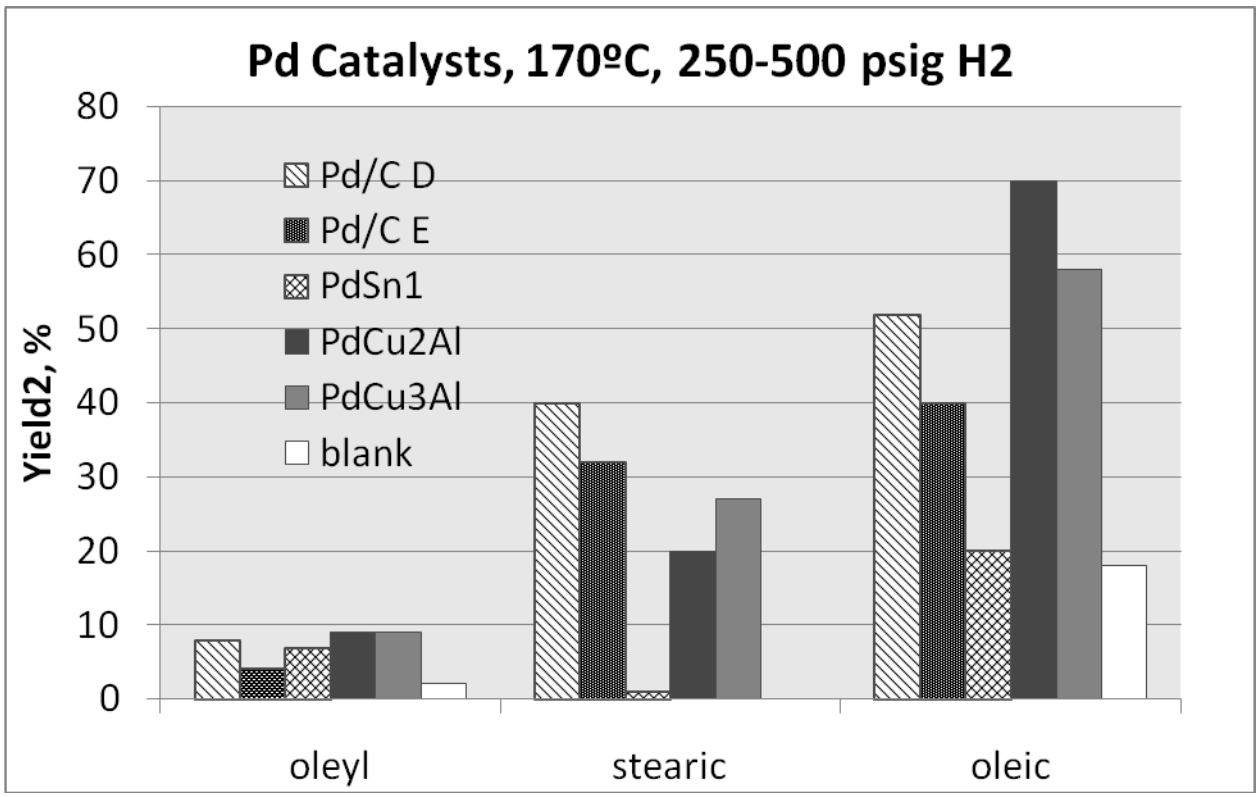

Figure 3.1a Comparison of Pd catalysts, reaction of linoleic acid.

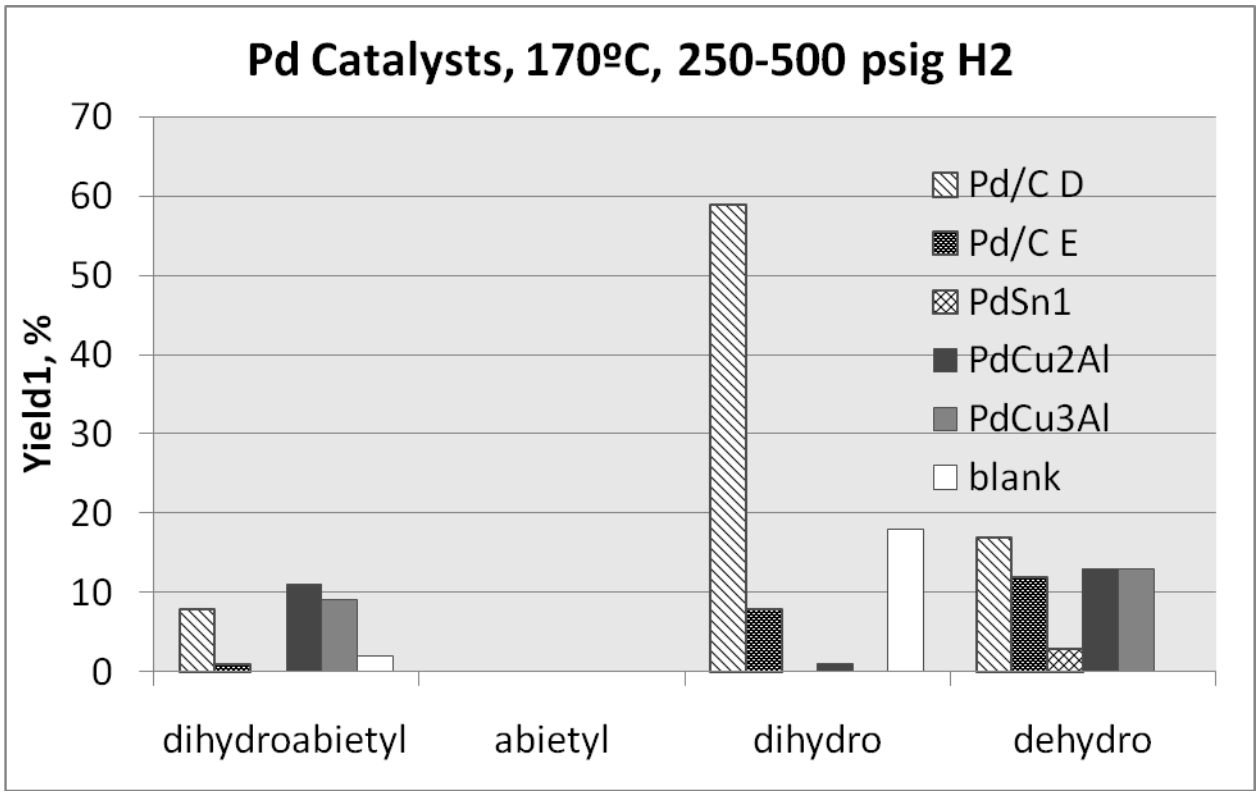

Figure 3.1b Comparison of Pd catalysts, reaction of abietic acid.

The other metallic catalysts were also compared at these baseline conditions, with results given in Figures 3.2a and 3.2b. These results suggest that the Co/B catalyst (I-25) is active and selective for fatty alcohol production. The Raney Ni or the supported Ru may be good catalysts for selective dehydrogenation of abietic to dehydroabietic acid. In contrast to some suggestions in the literature (Lombard and Ebelin, 1953), Raney Ni is not a good abietic acid hydrogenation catalyst compared to supported Pd. The activity of Pd/C for rosin acid hydrogenation is in agreement with Burgstahler et al. (1969). None of these catalysts showed promise for the production of rosin alcohols. The Pt alloy catalysts showed no remarkable characteristics; this was also true of a plain Pt/Al_2O_3 (PtAl1), and a plain Pd/Al_2O_3 (PdAl3), both of which were tested at other conditions.

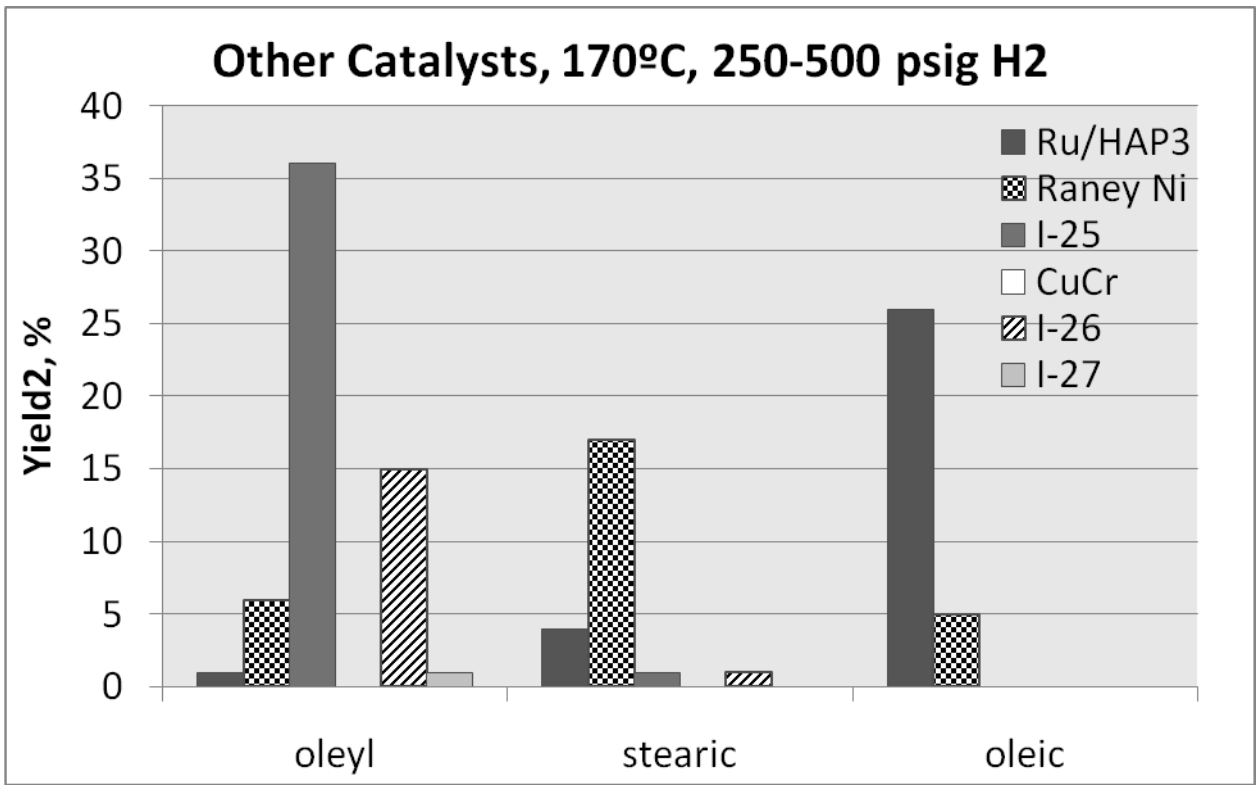

Figure 3.2a Comparison of other catalysts, reaction of linoleic acid.

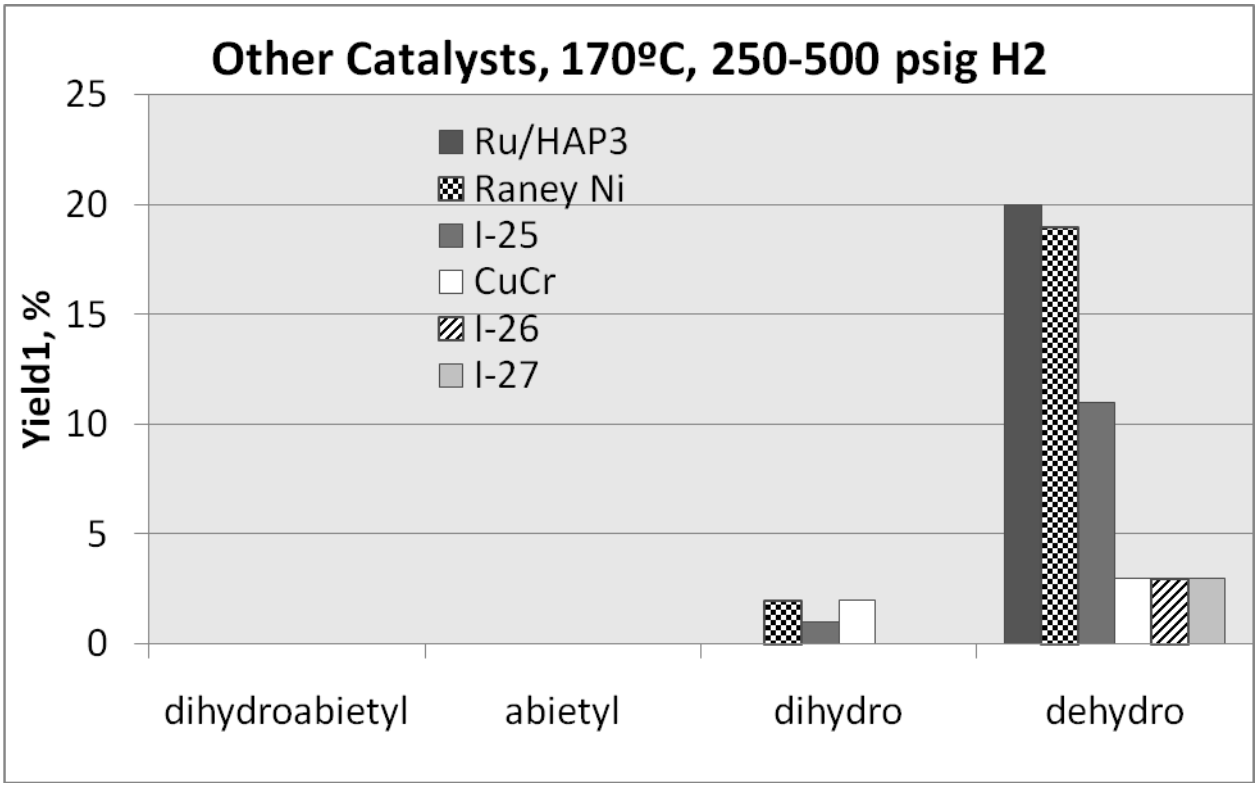

Figure 3.2b Comparison of other catalysts, reaction of abietic acid.

The literature on selective hydrogenations suggests that yields to alcohols can be improved if the reactions are conducted in slightly polar solvents, especially ethers and alcohols (Tahara et al., 1996). The acids are first converted to esters, which are more easily reduced (Hansley, 1947; Mugishima et al., 1957; Burgstahler et al., 1969). To test this possibility a series of reactions at 170ºC, 500 psig H_2 were conducted with catalysts thought to be selective for alcohol production from carboxylates, in 80 vol% ethanol. Results are shown in Table 3.2 below. The alcohols produced were a mixture of oleyl and linoleyl alcohols; no stearyl, abietyl, or dihydroabietyl alcohols were detected. The oleyl and linoleyl alcohols could not be adequately separated by the column (they also can't be distinguished by NMR), and so they are reported together. All of the catalysts were active and selective for fatty alcohols at these conditions, with slightly less selectivity obtained using the commercial copper chromate catalyst.

Table 3.2 Results of Synthetic DTO Hydrogenations in Ethanol Solvent

Run	Catalyst	Catalyst Composition, wt%	Y, % alcohol	Y, % other
Az9-1	I-25	75% Co/25% B	55	4
Az9-2	I-26	1% Pt/0.5% K/76% ZnO/Al_2O_3	65	3
Az9-3	I-27	1% Pt/1% ZnO/Al_2O_3	66	3
Az9-4	CuCr	2 $CuO•Cr_2O_3$	70	6

Finally, the literature on the synthesis of abietyl alcohol from abietic acid was examined; abietyl alcohol can be made at low temperature using a strong reducing agent in alcohol solvent (Scott and Hansley, 1938; Hansley, 1947). Two typical ester to alcohol reduction syntheses were duplicated in both ethanol and t-butanol solvents (Soai et al., 1984; Jagdale and Sudalai, 2008), but using the synthetic DTO feed as starting material.

The two step reaction procedure, using two different batches, was as follows. To 1 mL of the acid mixture, 1.7 mL of 25% tetramethylammonium hydroxide (TMAOH)/methanol was added, and then 12 mL ethanol to flask one and 12 mL t-butanol to flask two. The flasks were heated under N_2 for 30 min at ~40ºC. To flask one, 240 mg of $NaBH_4$ and 5 mg of $CoCl_2$ were added, with 2 mL of ethanol. This was reacted at 25ºC for 1 h, then at 40ºC for two more h. To flask two, 280 mg of $NaBH_4$ and use 2 mL of t-butanol was added, and it was reacted for 2 h at reflux (~85ºC). For both flasks the solvents were evaporated off in flowing N_2, and then the residues extracted six times with dichloromethane (10 mL apiece). A small amount of anhydrous sodium sulfate was added to the extracts, which were analyzed in this form by GC-MS.

Although the analysis proved difficult it appeared that the conversions of abietic acid to abietyl and the more hydrogenated alcohols was limited to ~17% yield for flask one and ~7% for flask two. So even with these presumably selective reduction conditions the alcohol selectivities from abietic acid are low with commercial tall oil. The production of such alcohols in the presence of either the fatty acids or their esters looks difficult, if not impossible, although it may be possible with stronger reducing agents such as $LiAlH_4$ or Na.

3.4 Dehydrogenation of Abietic Acid

This section focuses on the dehydrogenation of abietic acid to dehydroabietic acid. The commercial rosin acid feeds used throughout this analysis (HYR and TAO, Arizona Chemical) were first analyzed. GC-MS analysis of three separate samples of HYR showed that there was already a significant amount of dehydrogenated rosin acid present in this material, 25 mol% dehydrogenated product (consisting of molecular weights 300 and 298). There was 0.10% decarboxylated rosin. The oligomer analysis showed an average of 3.8 wt% combined dimer, trimer etc. The TAO gum rosin was analyzed in two separate samples from the bottle and seen to contain a minimum of 85% rosin acids, with 12 mol% dehydrogenated product (both molecular weights 300 and 298), but no decarboxylated rosin. The oligomer analysis showed an average of 11.6 wt% total oligomers.

3.4.1 Dehydrogenation of Abietic Acid in Small Bomb Reactors

Most of the early testing focused on screening catalysts. These tests were at 200ºC and H_2 pressures from 0 to 90 psig (with 30 psig N_2). Reaction times were kept to 1.5 h so the product slate could be kept relatively simple; the goal was to eliminate the worst catalysts before moving on to higher conversion conditions. These data were combined with some data at higher

temperature to generate the selectivity graphs shown below (Figure 3.3). In this figure the ratio of the dehydroabietic acid yield to the combined yields to all other products, both from abietic and linoleic acids, are computed. All data are for a dehydroabietic acid yield of at least 10%. All of the higher selectivities are for yields of at least 19%.

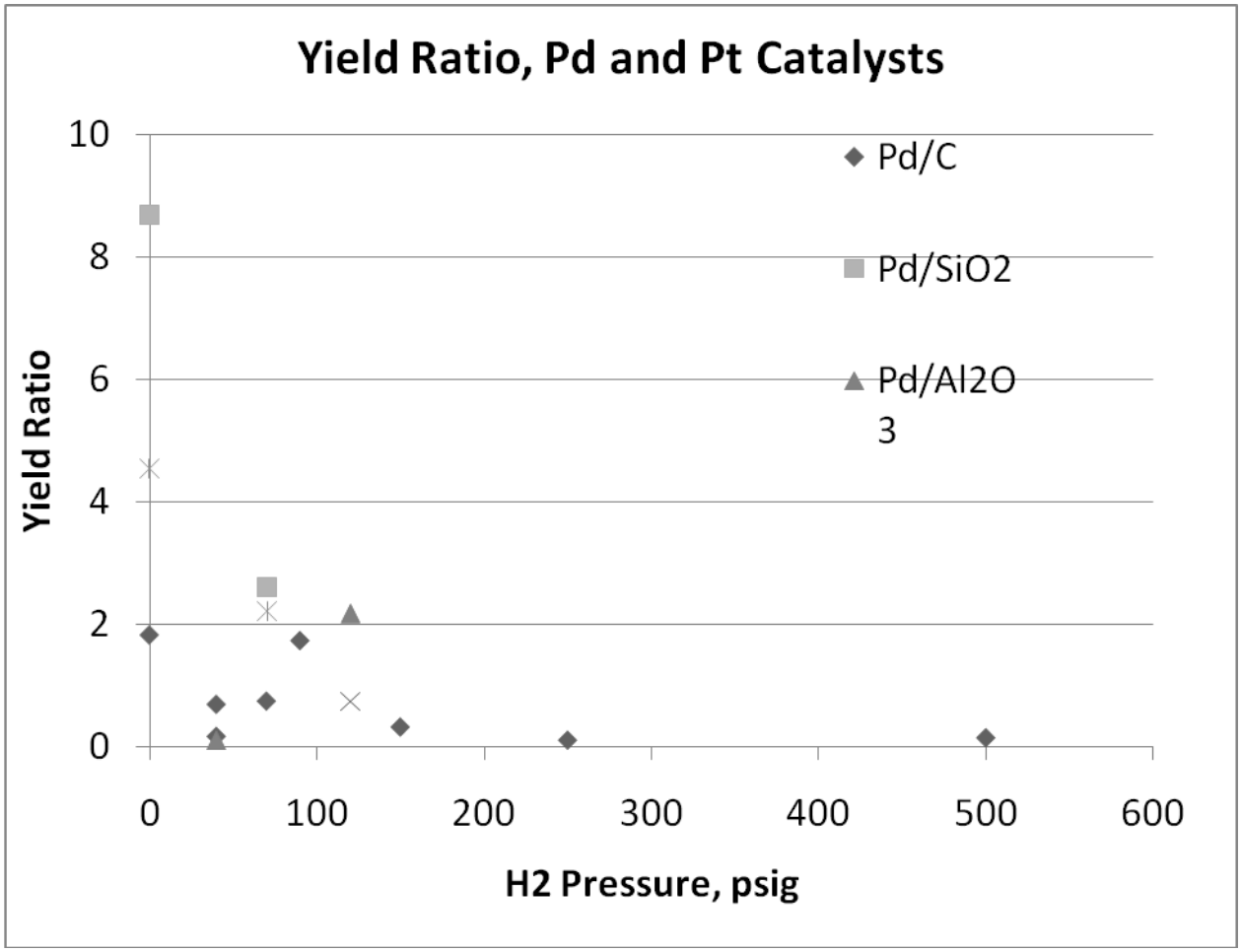

Figure 3.3a Comparison of simple Pd and Pt catalysts for selectivity to dehydroabietic acids. The yield ratio is the ratio of yield to dehydroabietic acid to the yield for all other products.

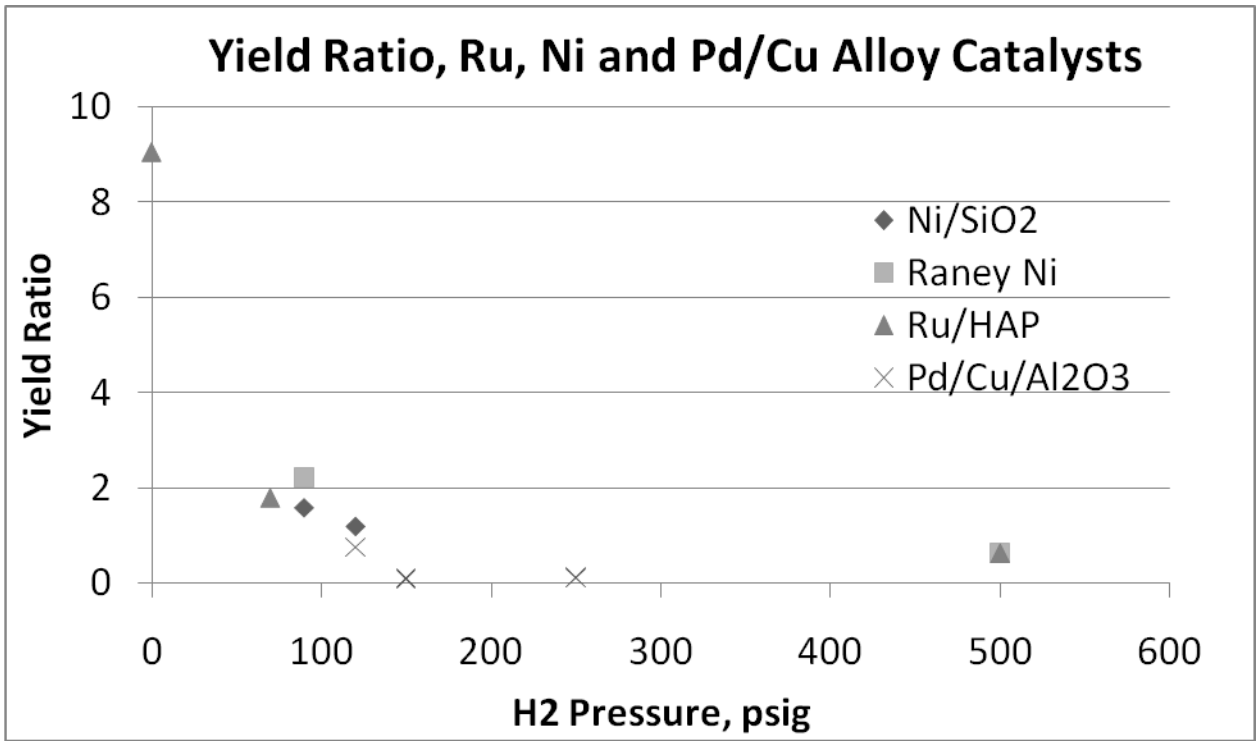

Figure 3.3b. Comparison of Ni, Ru and Pd/Cu catalysts for selectivity to dehydroabietic acids. The yield ratio is the ratio of the yield to dehydroabietic acid to the yield for all other products.

The results in Fig. 3.3a show that a silica support may prove useful here. The literature suggests a Pd/C catalyst will selectively dehydrogenate rosin acids (Song et al., 1985), and it does to some extent, although Pd/SiO_2 looks superior. The Ru/HAP (HAP = hydroxyapatite) catalyst also looks promising. The better performance of the silica and hydroxyapatite supports may be related to the more acidic nature of the silica and hydroxyapatite (the isoelectric point for silica is usually below pH = 3), or the generally higher dispersion of metal crystallites prepared on silica at high loadings, of which the results in Table 3.1 are representative.

From Figure 3.3 it would seem that no H_2 should be used here, but this can be deceiving. None of the catalysts were recycled, due to the small scale of the experiments (typically 0.1 g catalyst), so there could have been coke formation. Normally in any catalytic dehydrogenation,

some H_2 (maybe only a small partial pressure) is required to limit coking. Wang et al. (2009) suggest that at low N_2 pressures, hydrogenation, dehydrogenation and disproportionation of rosin acids will occur simultaneously over Pd/C catalyst. Larger-scale experiments as discussed later, with more catalyst and feed, resolved this question.

3.4.2 Equilibrium Analysis for Conversion to Dehydroabietic Acid

The maximum conversion to dehydroabietic acid was estimated from calculated equilibrium constants for the following reactions:

2 Abietic → Dehydroabietic + Dihydroabietic (reaction 1)

Abietic → Dehydroabietic + H_2 (reaction 2)

Abietic + O_2 → Dehydroabietic + H_2O (reaction 3)

Reaction 1, the disproportionation, was confirmed even in early work with catalysts (e.g., Fleck and Palkin, 1938), and has been re-confirmed several times since. This type of hydrogen transfer can also readily occur between abietic acid and fatty acids (Soltes and Zinkel, 1989), and between abietic and rosin acids with an exocyclic double bond (Song et al., 1985; Wang et al., 2009). If sufficient fatty acids or pimaric/isopimaric acids (have an exocyclic double bond) are present, it is generally agreed that 100% conversions are possible, i.e., the H_2 transfer reactions are irreversible at typical reaction conditions.

The equilibrium constants for reactions (1)-(3) were determined using heats and free energies of formation at 298.2 K. For the acids, these thermodynamic properties were estimated

by Joback's fragmentation method, as implemented in Cambridge Soft's ChemBioOffice 2010 (Table 3.3). All thermodynamic properties for the other compounds were taken from the NIST online database (2010). The equilibrium constants at temperatures other than 298.2 K were calculated by the van't Hoff equation, assuming the molar heat capacities for abietic, dehydroabietic and dihydroabietic acids are about the same.

Table 3.3 Estimated Thermodynamic Properties, Joback Method

Property	Value in kJ/mol, at 298.2 K
ΔH°f dehydro	-454.67
ΔH°f abietic	-521.32
ΔH°f dihydro	-587.97
ΔG°f dehydro	-57.07
ΔG°f abietic	-85.11
ΔG°f dihydro	-113.15

The equilibrium calculations all assume a feed composition equal to what we originally measured by GC-MS, i.e., 25 mol% (also ~25 wt %) dehydroabietic acids. Equilibrium calculations show that for reaction 1 the equilibrium constant is essentially temperature independent and the maximum conversion of abietic acid is 58%, corresponding to a composition of 47 mol% dehydroabietic. Calculations for reaction 2 show that in a flow system the equilibrium conversions would be 100% even with 5 atm (60 psig) H_2 in the feed. This is also true in a batch system at low pressures of H_2. But for a batch system at 5 atm (60 psig) H_2, the equilibrium conversions would be <100%, e.g., 74% at 200ºC and 94% at 250ºC. So from this analysis it appears that reaction (2) could occur, but the analysis says nothing about its

selectivity at a low (or zero) P_{H2} vs. either coking or disproportionation (reaction 1). Reaction (3) is irreversible at all temperatures of interest.

3.4.3 Dehydrogenation Results for Larger Reactors

In the dehydrogenation results for the larger-scale experiments the possibility of polymerization was taken into account and the data were corrected for it. The data are reported in terms of wt% dehydroabietic acid (uncorrected and corrected), ratio of dehydroabietic to the sum of abietic and dihydroabietic ($Y_{dehydro}$ in the tables below), wt% dimer, and wt% polymer. The uncorrected wt% dehydroabietic was determined from the GC-MS analysis, and the corrected wt% dehydroabietic was computed using both GC analyses, assuming a product average monomer molecular weight of 301 (the feed monomer average MW was ~302). Since both singly (d1), doubly (d2) and triply (d3) dehydrogenated products were found, and the monomer GC-MS analysis does not include dimer or trimer, the corrected wt% dehydro was computed as (basis = 1 mol monomer product)

$$wt\%\ dehydro = \frac{(mol\%\ d1)(300) + (mol\%\ d2)(298) + (mol\%\ d3)(296)}{\left[1 + \frac{wt\ \text{dimer}}{wt\ monomer} + \frac{wt\ trimer}{wt\ monomer}\right](301)} \quad \textbf{Eq(1)}$$

The molar ratio of rosin acid dehydrogenation to hydrogenation (D/H) was computed as:

$$D/H = \frac{(mol\%\ d1)(1) + (mol\%\ d2)(2) + (mol\%\ d3)(3)}{[mol\%\ dihydro\ ]} \quad \textbf{Eq(2)}$$

A D/H ratio higher than the feed suggests that the primary dehydrogenation reaction is either reaction (no O_2 present) or reaction (3) (O_2 present). A ratio much lower than the feed suggests that the primary dehydrogenation reaction is reaction (1).

In the polymer analysis, A dimer grouping between 18.5-23.5 min retention times and a trimer etc. grouping at times >25 min were observed. However, there were significant differences in the amounts of dimer with only slight differences in the initial temperature and heating rate on the injection port. In other words, the amount of dimer observed appeared to be sensitive to injector temperature, even for an on-column injection. This suggests the dimer is thermally labile. Also, some dimer was present in the HYR feed. In the calculations it was assumed that the dimer and polymer structures are the same as provided by Arizona Chemical (Locko, 2010), which are similar to the structures shown in Fujii et al. (1987). This dimer structure is shown below (Fig. 3.4).

There is also the problem of decarboxylation. The literature is contradictory on this point. Floyd (1952) specifically states that even at CO_2 pressures greater than 200 psig (14.6 atm) there is decarboxylation at 250ºC. In the first run cited in Table 1.1, the unsaponifiables (neutrals) increased from 4 to 9%. But Song et al. (1985) observed only 5% neutrals for the same reaction time, with a higher temperature (Table 1.1). No one else even mentions this as a problem. An increase in neutrals was observed by GC-MS, especially at 270ºC, to as high as 5.0% of the liquid mixture. But the vast majority of the samples were in the 1-3% neutrals range. Also, while running the glass reactors there was some condensed material, near the bottom of the condenser. This material was analyzed once (at the same conditions as run 17-5), and found to contain 44% neutrals, vs. 3.2% in sample 17-5 vs. 0.2% in the feed. The major

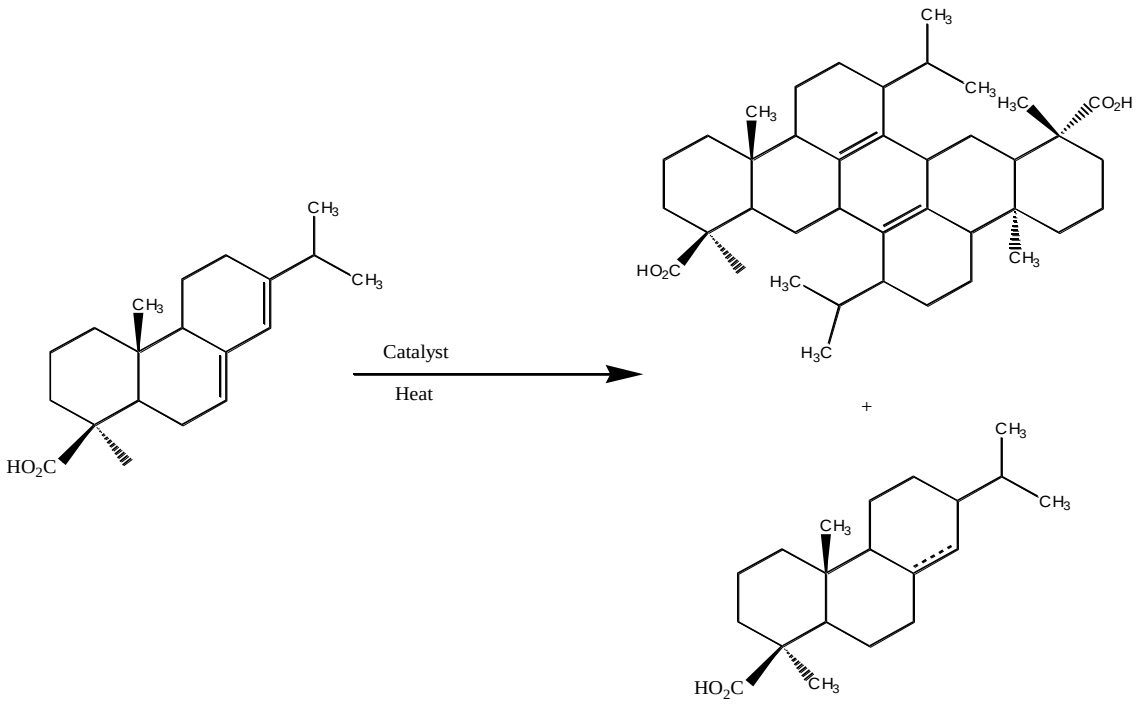

Figure 3.4 Reaction to dimer, according to Arizona Chemical and Fujii et al. (1987)

neutral produced was norabieta-7,13-diene (CAS number 57166-09-3, major fragments m/z = 55, 91, 105, 119, 161, 187, 243, 258, Otto and Simoneit, 2002), the simple decarboxylation product of abietic acid. So it appears that vapor losses through the condenser or the autoclave sample valve included a lot of neutrals. But given the high recoveries obtained in these experiments (94-96%, not accounting for the samples withdrawn), it is concluded that the decarboxylation products preferentially remained in the liquid phase. The bottom line is that if you cook a tall oil for too long at ~270ºC, there will be some decarboxylation.

The large-scale experiments focused on: (a) finding an optimal temperature range; (b) determining whether different gas environments influenced the results; (c) screening catalysts thought to be selective for dehydroabietic acid production based on past results in the smaller

bomb reactors; and (d) relative kinetics comparisons for the different catalysts. The more important results are shown in Tables 3.4 and 3.5. In the Tables, the weight ratio is feed/catalyst. Other experimental tests (not always shown in the tables) established the following.

- In an inert gas environment, there is little or no reaction without catalyst at <230ºC.
- The inert gas pressure did not influence the reactions.
- Reaction in an air environment without a catalyst is possible even at temperatures as low as 190ºC.
- Reaction with a Pd catalyst is slow at <230ºC, for any realistic feed/ catalyst weight ratios. Residence times >12 h would be required to reach 50% dehydroabietic. This is shown in Table 3.5, run #11, but it was confirmed in several other runs.

Table 3.4 Dehydrogenation Tests, Air, 1 atm

Run	t (h)	T (ºC)	Cat., wt. ratio	Y_{dehyd}	% dehyd	% dimer	% poly	Corr. %dehyd	D/H ratio
Feed				0.33	25	1.0	2.8	24	24
AzA3O-0	1	190	None	0.69	39	12.6[1]	0[1]	34	25
AzA5-1	3.7	180-190	None	0.50	33				29
AzA5-2	24	184	" "	1.07	49	10	0	43	47
AzA5-3	48	185	" "	1.58	56	6.6	3.8	50	55
AzA6-0	1	175	None	0.46	30				29
AzA10-3	1.5	190	Pd_S2, 200	0.48	32				5.6
AzA15-1	1	180	Pd/C E, 200	0.49	33				7.5
AzA15-2	2	200	" "	0.56	35	8.7	0.8	32	19

[1]Value provided by Don Scott, Arizona Chemical

The runs with air (Table 3.4) established that the oxidative dehydrogenation reaction (reaction 3) does take place slowly, but that considerable dimer and polymer will be produced with no catalyst present. The addition of catalysts does not affect the oxidative dehydrogenation much (runs 10 and 15). However, there is still dimer/polymer produced even with a catalyst. The much smaller D/H ratios observed when a catalyst was used suggest that the catalyst affects reaction (1), not both (1) and (3). It is possible that dimer production might decrease at higher temperatures, given the results in Table 3.5. But the major attraction of oxidative (vs. conventional) dehydrogenation is a lower reactor temperature, and this does not appear to be possible here.

Table 3.5 Dehydrogenation Tests, Inert Gas

Run	t (h)	T (°C)	Cat., wt. ratio	Y_{dehyd}	% dehyd	% dimer	% poly	Corr. %dehyd	D/H Ratio
Feed				0.33	25	1.0	2.8	24	24
AzA3-3	1	220	Pd/C E, 280	0.40	28	4.3[1]	0.2[1]	27	8.3
AzA4-1	1.7	230	Pd/C E, 240	0.59	37				6.0
AzA4-2	2.5	250	" "	0.65	38				4.3
AzA4-3	3.3	250	" "	0.76	42	16	3.1	34	3.8
AzA9-1	0.33	250	Pd/C E; 50	0.98	47				3.1
AzA9-2	0.67	245	'' ''	1.06	50	1.0	0.0	50	2.8
AzA9-3	1.0	232	'' ''	1.25	54	3.6	3.4	50	2.7

(Table 3.5 continued)

AzA9-4	0.5	230	“ “	1.13	52	3.8	2.5	49	2.4
AzA11-1[3]	17	203	Pd/C D; 100	0.63	38				4.9
AzA11-2[3]	24	202	“ “	0.75	42				3.8
AzA11-3[3]	44	201	“ “	0.87	46				3.0
AzA11-4[3]	68	225	“ “	1.19	53	1.9	3.1	50	2.3
AzA12-1	0.4	270	Pd/C E, 200	0.84	45	2.9	0.0	45	3.7
AzA12-2	0.35	300	“ “	1.98	65	2.9	0.0	62	3.3
AzA12-3	0.33	290	“ “	2.16	65				3.2
AzA12-9	2.0	270	“ “	3.25	67	2.1	2.9	64	3.0
AzA12-10	post[2]		“ “	2.48	69	4.0	3.4	63	2.7
AzA13-5	2.0	245-280	I-25, 150	0.43	29	2.3	0.9	28	17
AzA14-1[3]	2.0	250	Pd/C E, 67[4]	1.10	46				2.4
AzA14-2[3]	post[2]		“ “	1.38	56	3.5	1.7	53	2.7
AzA17-5	2.8	270	Raney Ni, 200	0.49	32	4.6	3.1	28	6.1
AzA18-3	4.70	250	Pd/C E, 400	1.65	60	4.4	3.3	55	3.4
AzA18-4	1.25	270	“ “	2.08	65	3.2	4.4	60	3.0

(Table 3.5 continued)

AzA18-5	post[2]		" "	1.98	62	3.2	4.4	57	2.8
AzA21-2[3]	0.5	270	Pd/C E, 400	0.86	42	3.4	2.4	40	3.8

[1]Value provided by Don Scott, Arizona Chemical
[2]After run completion and opening glass flask or autoclave
[3]Used CO_2 instead of N_2 as inert gas
[4]Re-used some of the catalyst from run A-11, without any intermediate pre-treatment

The runs without air (Table 3.5) suggest that the calculated maximum theoretical amount of dehydroabietic acid (assuming reaction (1), 47 mol% calculated maximum dehydroabietic) can be exceeded, even at 230ºC. From Table 3.5, it is seen that the feed D/H is very high (24), but the product D/H values at high conversion are in the 2-4 range, and always decrease with conversion. This suggests that reaction (1) predominates. The source of the excess conversion to dehydroabietic (above what is possible by reaction (1)) is likely H_2 transfer to the fatty acids and exocyclic rosin acids present – recall that these reactions are irreversible, and that there are ~5 wt% fatty and pimaric/isopimaric acids in the feed. Some reaction (2) may also occur, because the D/H ratio always remains >2; but it cannot be an important reaction.

While additional dehydrogenation takes place during the production of dimer and polymer (Fujii et al., 1987), some say the net production of H_2 by this route is negligible, because the dimer is subsequently hydrogenated (Loeblich and Lawrence, 1956). Therefore it was assumed that no net H_2 production was associated with dimer formation. The occurrence of reaction (2) to an extent much less than reaction (1) is in agreement with the D/H data of Song et al. and Wang et al. (1985, 2009, although neither drew this conclusion). Both of these studies also used Pd/C catalysts.

From Table 3.5 (Run 12), it looks as if the maximum wt% dehydro for this feed, in an inert gas environment, is around 62-64%, on a corrected basis. There is a definite, clear maximum, associated with the reaction equilibrium of (1) and the fatty and exocyclic acids in the feed. The presence of such a maximum is in agreement with Loeblich and Lawrence (1956) and Wang et al. (2009). The latter measured the activation energy of formation for dehydroabietic acid as 109 kJ/mol, which would imply a doubling of the reaction rate for every 15 K increase in temperature. From Table 3.5, the change in rate (as estimated using the conversion) is much slower at >260ºC, consistent with a reversible reaction approaching equilibrium.

The runs with a Co/B catalyst (run 13) and with Raney Ni (run 17) show that they are less active than Pd/C, by at least an order of magnitude. This result is consistent with previous dehydrogenation work showing that base metal catalysts are greatly inferior except in the presence of excess sulfur (Soltes and Zinkel, 1989).

With the exception of one sample from run 4 (an anomalous result), there are no large amounts of dimer produced. There is also no apparent trend in dimer/polymer formation. In fact, while there is an increase in the amount of dimer/polymer, it is limited to roughly double their total amount in the feed. This suggests that the dimer/polymer is thermal, not catalytic, in origin.

3.4.4 Kinetic Analysis for the Dehydrogenation Results

A first order (in total rosin acid) reversible reaction was assumed in order to obtain rate constants. Section 3.3.2 showed the existence of an equilibrium state characterized by <100% conversion for HYR, at all kinetically practical temperatures. The reaction would also be positive order in catalyst concentration, and was assumed first order. For such a reaction in an

isothermal batch reactor at constant catalyst concentration, the rate constant can be computed as in **Eq (3)**:

$$k = \frac{X_e}{C_c\left(t_2 - t_1\right)} \quad \ln\left[\frac{1-\left(\frac{X_1}{X_e}\right)}{1-\left(\frac{X_2}{X_e}\right)}\right] \qquad \textbf{Eq (3)}$$

Where C_c is the concentration of the catalyst, X_e is the reactant fractional conversion at equilibrium, X_1 is at time t_1, and X_2 is at time t_2. Because the catalyst concentration is inversely proportional to the wt liquid/wt catalyst, that ratio can be substituted for 1/Cc in the equation above. This makes the units on k simple (inverse time), as in a first-order overall reaction. All other conversion factors are absorbed into k. Some of the problems with this approach are discussed below.

A side-by-side comparison of the four catalysts with the two feeds (minus one run not completed, for reasons discussed below) is given below in Table 3.6.

Table 3.6 Kinetics Results, Dehydrogenation Tests

Run	**Feed**	**T(ºC)**	**Catalyst**	**Wt. ratio, Feed/cat.**	**% dimer etc.**	**% decarb.**	**Corrected % dehydro**	**k h^{-1}**
AzA3	HYR	220	Pd/C E	280	4.5[2]	0.14	27	9.4
AzA9[1]	HYR	230	Pd/C E	50	8.4	0.94	49	15
AzA18	HYR	250	Pd/C E	400	3.4	2.2	55	80

(Table 3.6 continued)

AzA18	HYR	270	Pd/C E	400	3.0	2.2	60	160
AzA12[1]	HYR	300	Pd/C E	200	5.5	1.2	60	270
AzA25	HYR	250	Pd/C M	200	4.2	0.69	50	69
AzA25	HYR	270	Pd/C M	200	7.0	3.5	58	59
AzA23	HYR	250	Pd/C B	200	8.0	3.5	37	19
AzA23	HYR	270	Pd/C B	200	9.1	4.6	51	37
AzA11	HYR	200	Pd/C D	100	5.0	1.8	50	0.61
AzA24	HYR	200	Pd/C D	200	8.9	3.2	55	73
AzA27	TAO	250	Pd/C E	200	7.4	0.77	68	810
AzA29	TAO	250	Pd/C M	200	8.2	0.63	67	500
AzA28	TAO	250	Pd/C B	200	7.4	2.2	65	370

[1]There were temperature control issues here – fluctuation around the values given in the Table.
[2]Value provided by Don Scott, Arizona Chemical.

The sources of error and their likely effects were examined. First, it is possible that the reaction is greater than first order in rosin acid because for the most part two rosin acid molecules are reacting (reaction (1)) in a transfer of H_2, sometimes called a "disproportionation". However, due to adsorption effects on the catalyst, the order of such a bimolecular reaction will

be less than two, so assuming first order behavior will not introduce major error. Second, in order to apply Eq. (2), X_e must be known; the maximum observed conversion (in any run) to dehydroabietic acid was used in order to estimate X_e. For HYR feed this is 64% and for TAO it is 68%. But the equilibrium conversion will change somewhat depending on how much oligomers and decarboxylated material are produced in the competing reactions. These amounts change from run-to-run, so there will be some bias in the estimated k's – e.g., the true k's are higher than the estimated k's in runs where a lot of oligomer or decarboxylated material is produced. The third source of error is in temperature control. In runs 9 and 12 there were temperature oscillations due to the difficulties with the high temperature (300ºC, run 12) or large amount of catalyst (wt. feed/wt. catalyst = 50, run 9). In runs 27-29 with the TAO feed there were also temperature spikes (to 268-285ºC) when the catalyst was added, with some gas evolution. These spikes were brief, and the temperature was back within 3ºC of 250ºC within 20 min. But due to the nonlinearity of the T-k relationship, for these TAO feed runs the true k's at the listed temperatures would be lower than the estimated values.

However, the values in Table 3.6 give an indication of the relative strengths and weaknesses of the four catalysts.

- "D" looks similar to "E", but makes more oligomer. Since it is supplied wet, it is more active than "E" on dry weight basis.
- "M" is also similar to "E", but it may not be able to survive temperature excursions – note the low k obtained in the test at 270ºC that immediately followed a test at 250ºC (run 25). It also appears to make more oligomer and more decarboxylated material.
- "B" is definitely less active than "E". However, "B" only contains 2 wt% Pd vs. 5 wt% Pd for "E". Taking the k for "E" (HYR feed) at 250ºC as ~80 h^{-1}, the ratio of (2/5)*80 = 32 h^{-1},

which is still higher than what was actually observed in the comparison test (for "B", 19 h^{-1} at 250ºC).

- Catalyst "B" also makes slightly more oligomer and decarboxylated material than "E" with HYR feed, and more decarboxylated material with TAO feed. The dehydrogenation reaction is catalyzed by the Pd, but it was concluded earlier that the oligomers could be thermal in origin (Section 3.3.3). It is also possible for the carbon surface to catalyze oligomerization or decarboxylation of rosin acids, since there are acid and base groups present on activated carbons (Figueiredo et al., 2007), and these are also known to affect the dispersion, and therefore the activity of Pd/C catalysts (Krishnakutty and Vannice, 1995; Albers et al., 1999). But there is no obvious correlation between the contact pH's (Table 3.1) and the amounts of oligomer or decarboxylates produced. There are more sophisticated and time-consuming ways to quantify the organic groups on carbons (Figueiredo et al., 2007); these tests might provide a better correlation.
- At this time all that can be concluded is that the greater amount of Pd in "E" (relative to B) favors the dehydrogenation over oligomerization and decarboxylation, based on the results in Table 3.6. This is true even though the nature of their surfaces are similar (slightly basic). While this hypothesis does not explain the anomalous oligomer result for run 9, given the sharp temperature excursion in this run there isn't enough certainty here to refute the other evidence. Overall, "E" is a better dehydrogenation catalyst.
- The oligomerization reactions look as if they can go either in the forward or reverse direction. Note that in some cases (especially with the TAO feed), there are fewer oligomers in the product than in the feed.

As discussed previously, a source of "excess" conversion to dehydroabietic acid (beyond the equilibrium of reaction (1)) is likely H_2 transfer to whatever fatty acids and exocyclic rosin acids are present in a feed. Recall that these reactions are irreversible, and that there are ~5 wt% fatty and pimaric/isopimaric acids in the HYR feed. The TAO feed was so reactive that there must be yet another factor here. The presence of a compound (~1%) in the TAO feed at MW = 286 was noted. The retention time and fragmentation pattern of this compound were consistent with abietinal (MW = 286.5); in the product samples there was also present (3-4% at 250ºC, <2.5% at 270ºC) a compound consistent with abietyl alcohol (MW = 288.5). Because aldehydes are notoriously unstable in heated GC injection ports, there may have been more abietinal actually in TAO. The hydrogenation of abietinal or of rosin acids to abietyl alcohol would also allow for more dehydrogenation (observed a maximum of 68%), and faster dehydrogenation (higher k's); both were observed with the TAO feed.

In general an increase in decarboxylated neutrals was observed from the GC-MS data, with respect to both time and temperature, to as high as 5.0% of the liquid mixture. Therefore the advantage of catalyst "E" over "B" is even more pronounced, because the only way to keep the batch times for both catalysts the same (other than use more of catalyst "B") would be to use a longer time or higher temperature. A higher temperature and/or longer time would mean more decarboxylates and more oligomer, based on the results in Table 3.6.

The alternative strategy would be to use a lower feed/catalyst ratio for "B". For example, a feed/catalyst weight ratio of 80 gives the same amount of total Pd atoms as a ratio of 200 for "E".

To calculate the % conversion at any time t for any catalyst, the following equation can be used,:

$$X = X_e \left[1 - \exp\left(-\frac{100\, k\, t}{X_e\, R_c} \right) \right] \qquad \textbf{Eq.(4)}$$

Where X is the % conversion of rosin acid to dehydrogenation product, X_e is the maximum (equilibrium) conversion, t is elapsed time, k is the first order rate constant in inverse time, and R_c is the weight ratio, feed/catalyst. Using the values in Table 3.6 and the X_e value for HYR feed, Figure 3.5 can be used to estimate the conversions to dehydrogenation products for catalysts "E" and "B" at weight ratio = 200.

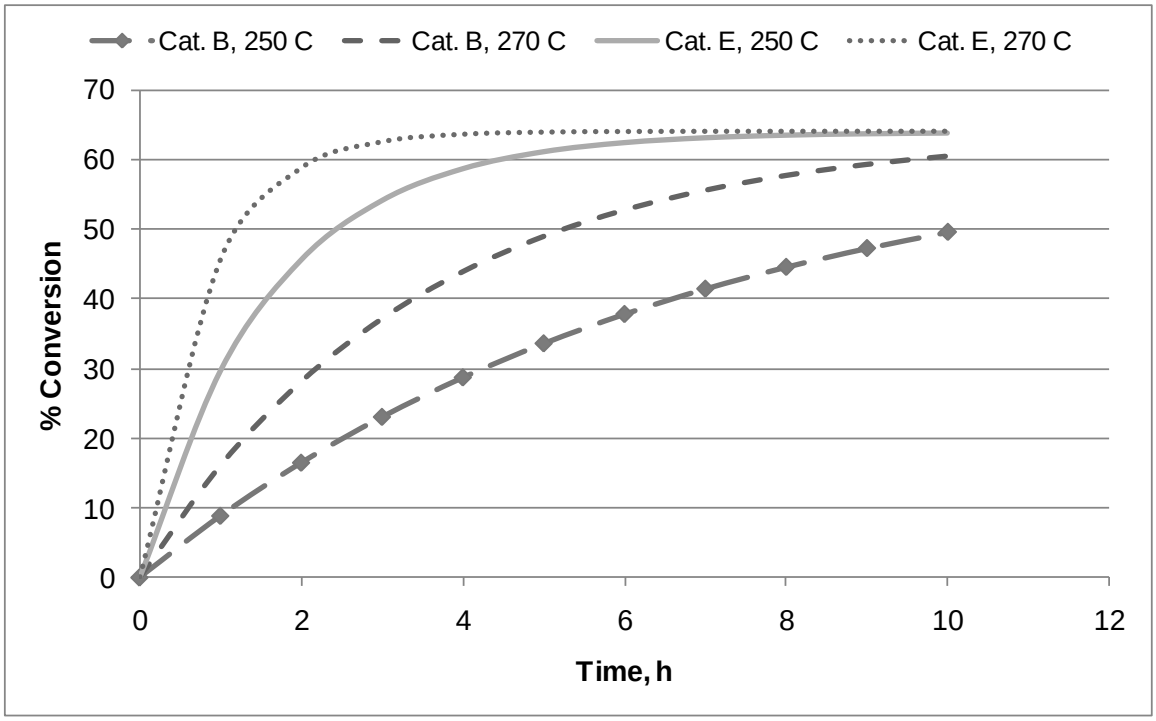

Figure 3.5 % Conversion to Dehydrogenation Products for Catalysts "B" and "E".

3.5 Selective Hydrogenations of Fatty Acids to Fatty Alcohols

The composition of the FA-1 fatty acid feed used in these experiments was confirmed by GCMS. The feed composition (mol%) is: stearyl alcohol – 1.5%; stearic acid – 1.9%; oleyl

alcohol – 0.1%; oleic acid – 48.8%; linoleic acid – 45.4%; linolenic acid – 0.4%; rosin and heavier fatty acids – 1.9%. Note especially the presence of some stearyl alcohol in the feed, which was confirmed by using a standard.

The calculation of the H_2 selectivity is somewhat difficult from these results. The procedures for fatty acid C=C bond hydrogenation for edible oils were followed, modifying them slightly to account for the alcohol production (Bussard, 231-232). Suppose only double bonds were hydrogenated; the reactions for the individual fatty acids linolenic (C18:3), linoleic (C18:2), oleic (C18:1) and stearic (C18:0) can be represented as:

$$\text{C18:3} \xrightarrow[H_2]{k_3} \text{C18:2} \xrightarrow[H_2]{k_2} \text{C18:1} \xrightarrow[H_2]{k_1} \text{C18:0}$$

Let the molar amounts of individual components C18:X be represented as M_{Xi}, where i = 0 for feed, i = 1 for product. The hydrogen consumption at each step of the reaction can be calculated.

1. Consumption of H_2 due to step 1 = x mol/L

$$x = M_{30} - M_{31} \quad \textbf{(5)}$$

2. Consumption of H_2 due to step 2 = y mol/L

Note that M_2 increases by amount x due to step 1, and decreases by amount y due to step 2. Hence the net decrease in M_2 is (y – x), giving:

$$y = (M_{20} - M_{21}) + x = (M_{20} - M_{21}) + (M_{30} - M_{31}) \quad \textbf{(6)}$$

3. Consumption of H_2 due to step 3 = z mol/L

Note that M_1 increases by amount y due to step 2, and decreases by amount z due to step 3. Hence the net decrease in M_1 concentration is (z – y), giving:

$z = (M_{10} - M_{11}) + y = (M_{10} - M_{11}) + (M_{20} - M_{21}) + (M_{30} - M_{31})$

Combining steps 1, 2 and 3, we get for total H_2 consumption (assuming no alcohols), $N_{H_2} = x + y + z$:

$$N_{H_2} = (M_{10} - M_{11}) + 2(M_{20} - M_{21}) + 3(M_{30} - M_{31}) \quad \textbf{(7)}$$

Let A_{xi} = the molar amounts of alcohols with x double bonds, again i = 0 for feed, i = 1 for product. Assume the alcohols are made through hydrogenation of the acids; then the total net H_2 consumption is:

$N_{H2} = (M_{10} - M_{11}) + 2\,(M_{20} - M_{21}) + 3\,(M_{30} - M_{31}) + (A_{01} + A_{11} + A_{21}) - (A_{00} + A_{10} + A_{20}) - (A_{11} - A_{10}) - 2\,(A_{21} - A_{20})$ **(8)**

Where the last two terms are needed to avoid double counting the H_2 used to hydrogenate the alcohols, which was accounted for in the first three terms as hydrogenating C=C's contained in acids. There is no linolenyl alcohol term, since none was observed. Simplifying eq. (8) gives:

$$N_{H2} = (M_{10} - M_1) + 2\,(M_{20} - M_2) + 3\,(M_{30} - M_3) + (A_{01} - A_{00}) + (A_{20} - A_{21}) \quad \textbf{(9)}$$

Finally, the hydrogenation selectivity to alcohols (% of reacted H_2 used just to make the alcohols) is given by:

$$S_{H2} = [(A_{01} + A_{11} + A_{21}) - (A_{00} + A_{10} + A_{20})]/N_{H2} \quad \textbf{(10)}$$

A comparison of the four Pd catalysts for hydrogenation of FA-1 is given below in Table 3.7. The FA feeds (except run F-5) were reacted at 87 bar (1250 psig), 220ºC, 3 h. The "V/W"

refers to the ratio of volume of substrate (FA-1) to weight of catalyst, mL/g. Run F-5 was run in the mini-autoclave at 68 bar (1000 psig), 220ºC, for 3 h. All final mixtures were solids at room temperature, confirming that the double bonds, and not the carbonyl groups, were selectively hydrogenated. No polymer was observed in the high temperature GC analysis.

Table 3.7 Kinetics Results, Hydrogenation with Pd Catalysts

Run	Catalyst	V/W	% stearyl	% oleyl	% stearic	% oleic	% linoleic	% dihydro-abietyl
	NONE	FEED	1.5	0.1	1.9	48.8	45.4	0
AzF-1	Pd/C M	10	1.4	0	23.4	64.6	5.5	3.1
AzF-2	Pd/C B	10	1.7	0	10.3	72.9	10.9	2.1
AzF-3	Pd/C E	10	1.5	0	27.1	62.7	6.2	0.2
AzF-4	Pd/C D	10	1.5	0.1	17.8	76.3	2.1	1.2
AzF-5	Pd/C B	200	2.3	0	74.2	19.7	0.2	0

From these results it was determined that simple Pd-based catalysts cannot be used for selective fatty acid hydrogenation; there is almost complete selectivity of the fatty acids for double bond hydrogenation. Conversely, there is good selectivity of the rosin acids to dihydroabietyl alcohol (in fact, little rosin acid was left in run F-1), so Pd/C-based catalysts may be a good fit here at these pressures.

The results for F-5 are interesting. The mini-autoclave is a reactor specifically adapted for multiphase hydrogenations, with a vortex stirrer that creates tiny gas bubbles. This results in (usually) higher rates of mass transfer for the H_2 to the catalyst. From Table 3.7 it is seen that a

much higher overall hydrogenation rate resulted – more than an order of magnitude higher once the weight ratio is considered. The 0% dihydroabietyl alcohol for run F-5 is not significant; essentially all of the rosin acids were hydrogenated here also, but it appears as if the final alcoholic products were more hydrogenated than dihydroabietyl alcohol, and they did not separate well from the fatty acids.

So the literature is correct in avoiding Pd-based catalysts for fatty acid hydrogenation at the carbonyl position. Much recent work has been on Ru/Sn/B and Co/Sn/B alloys. In initial work with FAMEs, Deshpande et al. (1990) found 91% selectivity to alcohol at 99% conversion for Ru-Sn/B_2O_3 and Narasimhan et al. (1989) found 89% selectivity at 68% conversion for Ru/Sn/α-Al_2O_3 (both at 270ºC, 45 bar, 40/1 substrate/catalyst). Toba et al. (1999) obtained ~70% selectivity at 100% conversion with Ru/Sn/Al_2O_3 at 240ºC and 65 bar. But all of these studies used saturated fatty acid feeds, so there was less of a selectivity issue. Therefore some of these alloy catalysts were prepared and tested for the fatty acid mixture FA-1. Even going to 250ºC, the conversions were slight (Table 3.8). The feed ratios (V/W) were 50 for all runs except F-6 (CuCr catalyst, V/W = 20). The balance of the product mixtures consisted of the rosin acids (some in the feed) and a small amount of unknowns. The H_2 selectivities to fatty alcohols were close to zero for the shorter time runs, and between 2 and 9% for the 8 hour runs.

Table 3.8 Kinetics Results, Hydrogenation with Alloy Catalysts (mol%)

Run	Cat.	T(ºC), t (h)	stearyl	oleyl	linoleyl	stearic	oleic	linoleic, linolenic
	FEED		1.5	0.1	0.0	1.9	48.8	45.8
AzF-6	CuCr	220, 3	1.5	0.5	0.0	4.1	58.4	33.5
AzF-7	Ru-HAP	220, 3	1.7	0.0	0.0	5.1	55.0	36.0

(Table 3.8 continued)

AzF-8	I-26	220, 3	1.6	0.0	0.0	2.1	50.6	43.6
AzF-9	I-27	220, 3	1.6	0.0	0.0	6.5	52.9	37.7
AzF-10	I-28	250, 3	1.7	0.3	0.1	5.0	58.2	34.0
AzF-11	I-29	250, 3	1.7	0.0	0.0	2.9	57.8	36.0
AzF-12	I-27	250, 3	1.5	0.0	0.0	3.1	52.2	41.6
AzF-13	I-26	250, 3	1.5	0.0	0.0	2.2	51.4	42.6
AzF-18	I-26	250, 8	2.3	0.4	0.1	8.9	63.8	15.8
AzF-19	I-27	250, 8	2.2	0.7	0.6	6.8	49.7	32.9
AzF-20	I-28	250, 8	1.9	0.5	0.1	18.2	54.5	20.9
AzF-21	I-29	250, 8	2.1	0.2	1.3	7.8	52.9	32.3

The literature suggests that fatty acid esters are more easily hydrogenated to the alcohols than fatty acids, and that the reactions are preferentially run in alcohol or ether solvents (or at least that such solvents leach less active metal). Therefore a combined hydrogenation and esterification was also examined, but first without any specific acid catalyst to promote the esterification. The experiments were of two types. In the first type of experiment, the reactor was loaded with 50% of the FA-1 feed and 50% methanol by volume. This mixture forms a single phase. The rest of the reaction procedure was unchanged, and all temperatures were 250ºC with pressures of 1250 psig (87 bar), except where noted.

Analyzing the reaction products with such a feed often required two separate analyses per sample, because the product mixtures were often two phase at ambient temperature: a light, mostly methanol phase; and a heavy phase containing most of the products. The two GC results were recombined to give a single composition estimate (Table 3.9), weighting them by volume

fraction on a methanol-free basis. The balance of the product mixture consisted of residual rosin acids, other heavies, or unknown.

Table 3.9 Kinetics Results, Hydrogenation with Alloy Catalysts and Methanol (mol%)

Run	Cat.	V/W	t (h)	stearyl	oleyl	linoleyl	stearic	oleic	linoleic, linolenic
	FEED			1.5	0.1	0.0	1.9	48.8	45.8
AzF-14	I-27	50	6	1.7	2.5	0	2.5	51.7	40.8
AzF-17	I-27	65	30	2.0	0.4	0	8.5	51.7	35.9
AzF-15	I-26	50	6	1.4	0.4	0	30.8	52.7	13.1
AzF-22	I-25	50	6	1.1	0	0	78.4	19.9	0
AzF-16	I-29	50	36	1.5	6.0	0	6.7	56.4	27.7
AzF-27	G22/2	50	26	2.7	1.2	0.8	10.9	55.9	25.9
AzF-29	Cu 1986T	50	4	2.6	0.1	0	7.0	48.6	39.7
AzF-29	" "	50	24	2.5	0.4	0.2	15.9	51.8	26.2
AzF-23[1]	I-27	25	29	1.8	0.7	0	33.7	52.5	9.1
AzF-24[2]	I-28	50	3	2.1	0.5	0	7.0	53.6	31.7
AzF-24[2]	I-28	50	28	2.0	0.4	0	10	69.0	15.6
AzF-25[2]	I-29	50	3	1.8	0.9	0	2.7	49.0	38.7
AzF-25[2]	I-29	50	30	2.1	0.8	0	11.2	52.5	30.0

[1]with 75% methanol and at 1100 psig (77 bar)
[2]at 1000 psig (70 bar)

The results showed that while adding the alcohol sometimes helped, still only I-27, I-29 and G22/2 (a commercial catalyst from Sud-Chemie containing 47 wt% CuO, 34% Cr_2O_3, 6% BaO, balance SiO_2) had even slight selectivity for the alcohols. The G22/2 was slightly better than the other commercial Cu/Cr oxide (Cu-1986T, from BASF, 35% Cu, 30% Cr, 3% Ba, 0.3% Mn, balance oxygen). Catalyst I-25 (Co/B alloy) was the most active for C=C hydrogenation. For alcohol selectivity, no benefit ensued upon extending the reaction time or increasing the amount of methanol. Only an increase in pressure seemed to increase the alcohol selectivity; the literature does sometimes quote H_2 pressures higher than used here, even with Ru-based catalysts. As these three classes of catalysts (copper chromates, Ru alloys with Sn, or Pt alloys with Zn) thought to be the most selective for carbonyl hydrogenation to alcohols (Corma, 2007), at least in the lower temperature/pressure range, it is doubtful that significant improvements in selectivity would ensue upon further variation in process conditions such as time or pressure, although a further increase in temperature may help (see below). All of the H_2 selectivities to fatty alcohols were ≤10%, except for runs 14 (30%, I-27) and 16 (18%, I-29).

The problem here could be insufficient esterification. To test this possibility, four runs were conducted with four typical esterification catalysts, measuring the extent of esterification. The four acid catalysts used were a MFI zeolite (H^+ form), an Amberlyst-type sulfonated PS-DVB resin (H^+ form), a tungstated zirconia (15% WO_3), and a supported heteropolyacid [$Cs_{2.5}H_{0.5}PW_{12}O_{40}\bullet 6H_2O$ (40 wt%)/SiO_2], all commercial materials used either industrially, in research, or both, as esterification catalysts. At typical catalytic esterification conditions (110ºC, 50% methanol, 100/1 mL/g V/W, N_2 blanketed) the percentages esterified in 3 h were: 33, 70, 40 and 34%. So from these results it was concluded that there probably was sufficient esterification in the runs in Table 3.9, given the higher temperatures/longer times of these runs,

and given that the supported metal catalysts also possess some esterification activity (Tahara et al., 1997; Taniguchi et al., 2011; Pouilloux et al., 1998).

But to be certain, two more runs were conducted using both types of catalysts (acid plus hydrogenation) at the same time, using hydrogenation catalyst I-27. In run F-26 the Amberlyst-type sulfonated PS-DVB resin was added, while in F-28 the tungstated zirconia was added. Equal weights of the two catalyst types were used, at 50/1 mL/g total catalyst W/V, 50% methanol, 250ºC, and 1250 psig (87 bar). These results are in Table 3.10.

The final H_2 selectivities to fatty alcohols in both runs were <5%. The results suggest that further promotion of the esterification reaction by adding acid catalysts does not shift the selectivities away from C=C bond hydrogenation.

Table 3.10 Hydrogenation with Alloy and Acid Catalysts, and Methanol (mol%)

Run	Hydrog. Cat.	t (h)	stearyl	oleyl	linoleyl	stearic	oleic	linoleic, linolenic
	FEED		1.5	0.1	0.0	1.9	48.8	45.8
AzF-26	I-27	3	2.7	0.0	0.2	3.6	50.5	39.9
AzF-26	I-27	25	2.3	0.1	0	13.0	63.0	17.1
AzF-28	I-27	4	2.5	0.7	0.1	3.1	47.0	43.4
AzF-28	I-27	28	2.8	0.3	0.7	6.4	56.0	31.6

In conclusion, fatty acids or their esters cannot be selectively hydrogenated at 250ºC or less and 87 bar or less, using any of several carbonyl hydrogenation catalysts in reasonable substrate/catalyst ratios. Comparing these data to others', it is further concluded that the key to higher alcohol selectivities with alloy catalysts is both higher temperatures and a more thorough examination of the catalyst preparation procedures, especially regarding their initial reduction

with H_2. According to the literature a mixture of stearyl and oleyl products will always be obtained, even at low conversions. The Cognis and Henkel patents (e.g., Cu-Zn oxides, >270 bar, 220ºC, Pelzer et al., 2004; Zn-Cr oxides, >250 bar, 300ºC, Demmering et al., 2004) appear to represent the state of the art.

In these experiments, the total yield to alcohols did not exceed 8%, using a 3% $Ru/Sn/TiO_2$ catalyst (2/1 molar Sn/Ru). This was not exceeded with any other catalyst, including the newer commercial Cu-Cr catalysts. The $Ru/Sn/TiO_2$ and $Ru/Sn/Al_2O_3$ are literature catalysts that are supposed to be very active for ester to alcohol hydrogenations. They are not commercial due to the expense of Ru. Quite a bit of other hydrogenation (linoleic --> oleic --> stearic) did take place over these catalysts; however, the Co/B- and Pt/Zn-based catalysts were even more active for these reactions, and so less selective for hydrogenation to fatty alcohols.

The poor selectivities to fatty alcohols were somewhat surprising given previous results for $Ru/Sn/Al_2O_3$ catalyzing the hydrogenation of rosin acids to rosin alcohols, at similar conditions, with >80% selectivity (Tahara et al., 1996, 1997). Possibly the catalysts are more selective in the presence of particular solvents (Tahara et al. used ~2/3 diglyme); more likely, the rosin C=C bonds are harder to hydrogenate than the C=C bonds in the fatty acids. Also, in Tahara et al.'s work very large, impractical catalyst amounts were used.

But there are three literature instances where methyl oleate was used as a reactant (Tahara et al., 1997; Pouilloux et al., 1998; Pouilloux et al., 2000), giving alcohols selectively. The first of these quotes complete conversion at 260ºC with 76% yield to stearyl alcohol, using 1:1 molar $Ru/Sn/Al_2O_3$. The second quotes a conversion of 75%, with 49% selectivity to the unsaturated alcohols, at 270ºC and 40 bar H_2, using $Co_{2.2}Sn_{4.3}B_{0.5}/Al_2O_3$. The third quotes 80% conversion and 41% selectivity for a similar catalyst at 270ºC and 80 bar H_2.

So it is possible that these preparations just did not duplicate the most selective catalysts. Tahara et al. (1997) and Silva et al. (2009) stress the importance of excess Sn leading to Sn reduction to form RuSn intermetallics, so the next step might be to try higher reduction temperatures for the Ru/Sn catalysts. But Pouilloux et al. (2000) and Toba et al. (1999) stress that higher reaction temperatures and M/Sn near 1 actually lead to higher alcohol selectivities; both concluded that there was no Sn^0 in the active catalyst, and both kept the initial reduction temperatures relatively low. Possible future work would therefore be to prepare and test Co/Sn/B (Co/Sn = 1) materials instead of Ru/Sn (which Pouilloux et al. claim do not work as advertised), and also do some experiments at higher reaction temperatures.

Most of the patents deal with process schemes, and do not give much insight into either reaction conditions or catalysts. In most of them, Cu-Zn, Zn-Cr or Zn-Al-based commercial catalysts were used at 250-300ºC and 200 bar or higher for (usually) the FAMEs (e.g., Demmering et al., 2004; Pelzer et al., 2004; Nakaoka and Mototani, 2009). A slight exception is the patent by Tamura et al. (1998), which claims high unsaturated alcohol selectivity with ZnO/Y_2O_3 and other rare-earth oxide catalysts, but also at pressures >200 bar and temperatures >250ºC.

There is also some very recent work on aldehyde (citral) to unsaturated alcohol hydrogenations, quoting selectivities in the 30% range at modest conditions (no solvent, 50ºC, 50 bar H_2, turnover frequencies >0.01 s^{-1}, Alvarez-Rodriguez et al. 2011). The catalysts are Pt/RE/K/L zeolites, where RE = a trivalent rare earth cation such as La^{3+}. These unsaturated alcohol selectivities are near what is found for citral hydrogenation with state-of-the-art homogeneous Ru catalysts (Melean et al., 2011), but without the complications of excess solvent, biphasic media, phase transfer agents, and the price of Ru.

CHAPTER 4: CONCLUSIONS

The results for the selective hydrogenation of abietic acid showed that no typical hydrogenation catalyst could give a high yield and selectivity for abietyl alcohol at the conditions examined. Poor yields and selectivities were obtained even when using sodium borohydride as the reducing agent at low temperature. It is possible that stronger reducing agents could be used; however, such reactions would likely be unsuitable for large scale manufacturing processes.

The dehydrogenation of abietic acid to dehydroabietic acid was successful for many common hydrogenation catalysts. The Pd/C class showed the highest activity, and of the different activated carbon supports used, the ones with more basic groups (higher contact pH) seemed to provide the best results, based on an evaluation of activity, polymerization selectivity and decarboxylation selectivity. The decarboxylation increased when the time or temperature was increased significantly. From the data contained in Table 3.5, for a batch reactor using Pd/C "E" with a Feed/catalyst weight ratio of approximately 200, it would take about 2 to 2.5 hours to reach the dehydrogenation equilibrium at 270^{o}C. At 250^{o}C it would take 4 to 5 hours, with slightly less decarboxylation and polymerization. The reaction was shown to be almost nonexistent at temperatures less than 230^{o}C.

The dehydrogenation of abietic acid predominantly occurs by disproportionation, and will reach an equilibrium conversion of 58% in a feed comprised of predominately abietic acid. The equilibrium percent yields and reaction rates will increase with the amount of H_2 acceptors, such as rosin acids with exocyclic bonds (e.g. pimaric acid), rosin aldehydes, fatty acids or alcohols. But the gas environment in such reactions did not exhibit a significant effect. Finally, the polymer observed in both the feed and the product was determined to be thermally rather than catalytically produced based on its non-varying concentrations with respect to catalyst type.

The polymer is also thermally labile, as observed by its variation with the GC injector temperatures.

Selective hydrogenation of unsaturated fatty acids to unsaturated fatty alcohols with small amounts of rosin acids present is not possible with commercial hydrogenation catalysts used at conditions less than 270^{o}C and 1500 psig hydrogen. Possible further work in this area would include changing the catalyst reduction temperatures, exploring different solvents and changing the metal to Sn ratio in the catalysts.

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APPENDIX A

GAS CHROMATOGRAPH (GC) AND MASS SPECTRUM (MS) DETAILS

Table A.1 The Parameters for Sylv4 (the GC/MS method that was used to analyze the runs for hydrogenation of abietic acid.)

Initial Temperature	150°C
Initial Time	5 min
Ramp	5°C/min
Hold Temperature	185°C
Hold Time	5 min
Second Ramp	4°C/min
Final Temperature	230°C
Final Time	14 min
Carrier Gas Retention Time	1.128 min
Septum Purge	3 mL/min
Purge On Time	2 min
Split Rate	33 mL/min
Injector Temperature	280^{o}C
Detector Temperature	230^{o}C
Amount Injected	0.3 μL

Table A.2 The Parameters for Sylv42 (the GC/MS method that was used to analyze the runs for the dehydrogenation of abietic acid.)

Initial Temperature	140°C
Initial Time	7 min
Ramp	5°C/min
Hold Temperature	185°C
Hold Time	5 min
Second Ramp	4°C/min
Final Temperature	230°C
Final Time	14 min
Carrier Gas Retention Time	1.128 min
Septum Purge	3 mL/min
Purge On Time	2 min
Split Rate	33 mL/min
Injector Temperature	280^{o}C

(Table A.2 continued)

Detector Temperature	230°C
Amount Injected	0.3 μL

Table A.3 The Parameters for AzFAME3 (the GC/MS method that was used to analyze the runs for the hydrogenation of Fatty Acid.)

Initial Temperature	120°C
Initial Time	0 min
Ramp	2°C/min
Hold Temperature	130°C
Hold Time	0 min
Second Ramp	1°C/min
2nd Hold Temperature	140°C
2nd Hold Time	0 min
3rd Ramp	4°C/min
Final Temperature	220°C
Final Time	12 min
Carrier Gas Retention Time	1.128 min
Septum Purge	3 mL/min
Purge On Time	0.5 min
Split Rate	33 mL/min
Injector Temperature	280°C
Detector Temperature	230°C
Amount Injected	0.2 μL

Table A.4 The Parameters for Az9 (the GC/FID method that was used to analyze the amount of rosin polymerization in all experiments.)

Initial Temperature	40°C
Initial Time	0 min
Ramp	10°C/min
Hold Temperature	160°C
Hold Time	10 min
Second Ramp	15°C/min
Final Temperature	380°C
Final Time	20 min
Carrier Gas Flowrate	6mL/ min
Injector Temperature	40°C
Injector Ramp	15°C/min
Injector Final Temperature	380°C
Detector Temperature	380°C
Amount Injected	0.2 μL

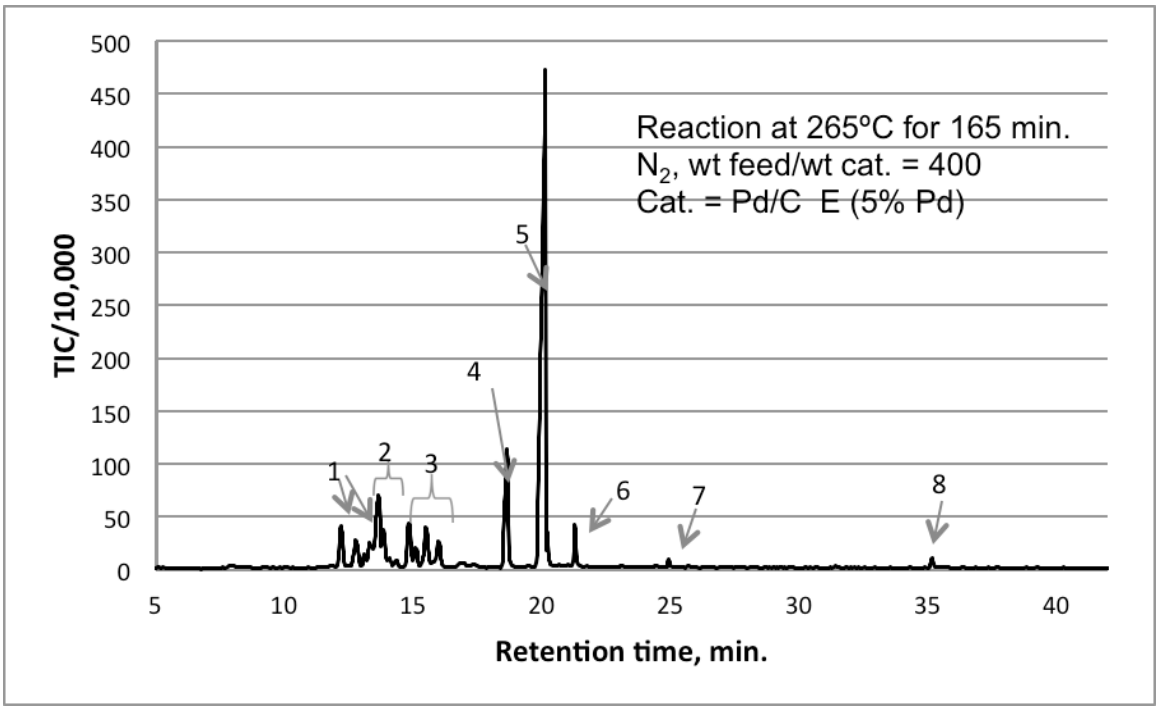

Figure A.1 Chromatogram of 18-2A from the Dehydrogenation Runs

1 Abietic Acid isomer

2 Dihydroabietic

3 Abietic Acid isomers

4 Abietic Acid

5 Dehydroabietic

6 Dehydro-Dehydroabietic

7 Dehydro-Dehydroabietic

8 MW =328

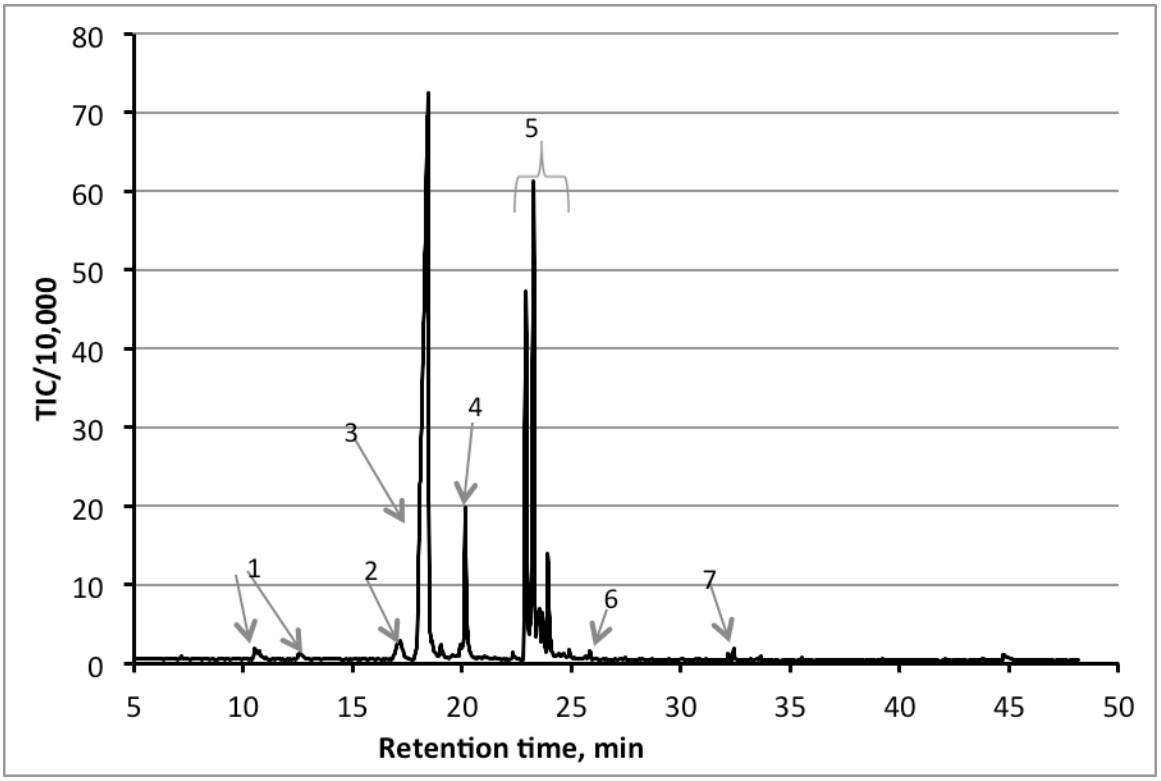

Figure A.2 A Chromatogram of FA-1(The Fatty Acid Feed)

1 Stearyl Alcohol

2 Stearic

3 Oleic

4 Linoleic

5 Linoleic

6 Abietic

7 Assorted Rosin Acids

APPENDIX B

TABULAR REACTION DATA AND RESULTS

Table B.1 Bomb Reactor Raw Data – Hydrogenation of Abietic Acid

Run #	Catalyst	wt.	Red. Tube P,	Red. T,	Red. / Rxn Gas	Feed Vol.,	Rxn P	Rxn T	Rxn Time,
		g	psig	^{o}C		mL	psig	^{o}C	hr
Az-1-1	PtAl1	0.2	100	150	40% H_2	2	100	200	2
Az-1-2	Pd/C E	0.2	100	150	40% H_2	2	100	200	2
Az-1-3	PdAl3	0.2	100	150	40% H_2	2	100	200	2
Az-1-4	NiSi1	0.2	100	150	40% H_2	2	100	200	2
Az-2-1	PtAl1	0.2	100	150	40% H_2	2	100	250	1
Az-2-2	Pd/C E	0.2	100	150	40% H_2	2	100	250	1
Az-2-3	PdAl3	0.2	100	150	40% H_2	2	100	250	1
Az-2-4	NiSi1	0.2	100	150	40% H_2	2	100	250	1
Az-3-1	PtAl1	0.2	100	120	40% H_2	2	300	120	1
Az-3-2	Pd/C E	0.2	100	120	40% H_2	2	300	120	1
Az-3-3	PdAl3	0.2	100	120	40% H_2	2	300	120	1
Az-3-4	NiSi1	0.2	100	120	40% H_2	2	300	120	1
Az-3-7	CoSi1	0.2	100	120	40% H_2	2	300	120	1
Az-4-1	Pd/C E	0.2	150	170	H_2	2	150	170	2.5
Az-4-2	PdCu2Al1	0.1	150	170	H_2	2	150	170	2.5
Az-4-3	PdCu3Al1	0.1	150	170	H_2	2	150	170	2.5
Az-4-4	PdSn1	0.1	150	170	H_2	2	150	170	2.5
Az-5-1	Pd/C E	0.2	300	120	40% H_2	2	300	120	1
Az-5-2	PdCu2Al1	0.1	300	120	40% H_2	2	300	120	1
Az-5-3	PdCu4Al1	0.1	300	120	40% H_2	2	300	120	1
Az-5-4	PdSn1	0.1	300	120	40% H_2	2	300	120	1
Az-6-1	Pd/C D	0.2	200	170	H_2	4	250	170	1.5
Az-6-2	PdCu2Al1	0.1	200	170	H_2	4	250	170	1.5
Az-6-3	PdCu3Al1	0.1	200	170	H_2	4	250	170	1.5
Az-6-4	Blank	-	-	-	H_2	4	250	170	1.5
Az-7-1	Pd/C D	0.1	150	170	H_2	4	500	170	1
Az-7-2	PdSn1	0.1	150	170	H_2	4	500	170	1
Az-7-3	Raney Ni	0.2	150	170	H_2	4	500	170	1
Az-7-4	Ru/HAP-3	0.1	150	170	H_2	4	500	170	1
Az_8-1	I-25	0.1	500	170	H2	4	500	170	1
Az_8-2	I-26	0.1	500	170	H_2	4	500	170	1
Az_8-3	I-27	0.1	500	170	H_2	4	500	170	1

(Table B.1 continued)

Az_8-4	CuCr	0.2	500	170	H_2	4	500	170	1
Az_9-1	I-25	0.1	500	170	H_2	1 +4 EtOH	500	170	1
Az_9-2	I-26	0.1	500	170	H_2	1 +4 EtOH	500	170	1
Az_9-3	I-27	0.1	500	170	H_2	1 +4 EtOH	500	170	1
Az_9-4	CuCr	0.2	500	170	H_2	1 +4 EtOH	500	170	1
Az_10-1	Blank	-	-	-	H_2	2	120	202	1.67
Az_10-2	NiSi1	0.1	150	170	H_2	2	120	202	1.67
Az_10-3	Pd/C E	0.1	150	170	H_2	2	120	202	1.67
Az_10-4	Raney Ni	0.34	150	170	H_2	2	120	202	1.67
Az_11-1	Pd/C D	0.2	150	260	H_2	2	100	200	1.5
Az_11-2	PdS2	0.1	150	260	H_2	2	100	200	1.5
Az_11-3	PtS2	0.1	150	260	H_2	2	100	200	1.5
Az_11-4	Ru/HAP-3	0.1	150	260	H_2	2	100	200	1.5
Az_12-1	Pd/C D	0.2	150	260	H_2	2	90	200	1.5
Az_12-2	PdS2	0.1	150	260	H_2	2	90	200	1.5
Az_12-3	PtS2	0.1	150	260	H_2	2	90	200	1.5
Az_12-4	Ru/HAP-3	0.1	150	260	H_2	2	90	200	1.5
Az_13-1	Blank	-	-	-	H_2	2	90	250	1.5
Az_13-2	Pd/C D	0.199	150	260	H_2	2	90	250	1.5
Az_13-3	Pd/C E	0.099	150	260	H_2	2	90	250	1.5
Az_13-4	Pd S2	0.105	150	260	H_2	2	90	250	1.5
Az_14-1	Raney Ni	0.307	150	260	H_2	2	90	250	1.5
Az_14-2	NiSi1	0.114	150	260	H_2	2	90	250	1.5
Az_14-3	Pd/C D	0.106	150	260	H_2	2	90	250	1.5
Az_14-4	CDX5(3)	0.105	150	260	H_2	2	90	250	1.5

The balance for the 40% H_2 was made up with N_2

Table B.2 Raw Results for the Large Scale Dehydrogenation Reactions (Autoclave and Glass Reactors)

Run	Pressure	Gas	Feed Amount	Catalyst	Catalyst Amount	Feed
	psig		mL		g	
Az_A1	90	N_2	100	Pd/C E	0.65	NCY
Az_A2	30	Ar	500	Pd/C E	2.5	NCY
Az-A3	30	N_2	140	Pd/C E	0.5	HYR
Az--A4	90	N_2	120	Pd/C E	0.5	HYR
Az-A5	-	-	38	-	0	NCY
Az-A6	-	-	460	-	0	NCY
Az-A7	-	Ar	98	-	0	HYR
Az-A8	-	Ar	102	Pd-S2	0.505	HYR
Az-A9	-	Ar	100	Pd/C E	2	NCY
Az-A10	-	Air		Pd-S2	.505	HYR
Az-A11	30	N_2/CO_2	148	Pd/C D	1.49	HYR
Az-A12	-	N_2	100	Pd/C E	.503	HYR
Az-A13	-	N_2	100	I-25	.647	HYR
Az-A14	120	CO_2	100	Pd/C D	1.49	HYR
Az-A15	-	sparging air	100	Pd/C E	0.49	HYR
Az-A16	-	N_2	100	I-25	.647	HYR
Az-A17	-	N_2	100	raney Ni	.548	HYR
Az-A18	-	N_2	100	Pd/C E	.257	HYR
Az-A19	-	N_2	100	NiSi1	.246	HYR
Az-A20	-	N_2	100	2%Pd/C B	.494	HYR
Az-A21	-	CO_2	150	Pd/C E	.376	HYR
Az-A22	-	N_2	100	Pd/C D	.499	HYR
Az-A23	-	N_2	100	2%Pd/C B	.5012	HYR
Az-A24	-	N_2	100	Pd/C D	.4993	HYR
Az-A25	-	N_2	200	MPT-5	1.005	HYR
Az-A26	-	N_2	100	Ru HAP-3	0.495	HYR
Az-A27	-	N_2	100	Pd/C E	.499	TAO
Az-A28	-	N_2	100	2%Pd/C B	.508	TAO
Az-A29	-	N_2	100	MPT-5	.4987	TAO

Table B.3 Raw Results for Fatty Acid Hydrogenation Experiments

Run #	Catalyst	Amount Catalyst	Red. Tube P	Red. T	Feed Vol.	Rxn P	Rxn T	Rxn Time
		g	psig	^{o}C	mL	psig	^{o}C	hr
AzF-1	MPT-5	0.991	-	-	10	1250	220	3
AzF-2	2% Pd/C B	1.017	-	-	10	1250	220	3
AzF-3	Pd/C E	1.036	-	-	10	1250	220	3
AzF-4	Pd/C D	1.007	-	-	10	1250	220	3
AzF-5	2% Pd/C B	0.0649	-	-	13	1000	220	3
AzF-6	CuCr	0.5003	500	220	10	1250	220	3
AzF-7	Ru-HAP	0.2013	500	220	10	1250	220	3
AzF-8	I-26	0.1994	500	220	10	1250	220	3
AzF-9	I-27	0.1987	500	220	10	1250	220	3
AzF-10	I-28	0.205	500	220	10	1250	250	3
AzF-11	I-29	0.2013	500	220	10	1250	250	3
AzF-12	I-27	0.194	500	220	10	1250	250	3
AzF-13	I-26	0.1998	500	220	10	1250	250	3
AzF-14	I-27	1.0105	-	-	50*	1250	250	6
AzF-15	I-26	0.9987	-	-	50*	1250	250	6
AzF-16	I-29	1.0015	-	-	50*	1200	250	36
AzF-17	I-27	0.1408	-	-	6.5*	1200	250	30
AzF-18	I-26	0.209	-	-	10	1200	250	8
AzF-19	I-27	0.201	-	-	10	1200	250	8
AzF-20	I-28	0.203	-	-	10	1200	250	8
AzF-21	I-29	0.205	-	-	10	1200	250	8
AzF-22	I-25	1.009	-	-	50*	1250	250	6
AzF-23	I-27	1.492	-	-	75^	1100	250	29
AzF-24	I-28	1.0105	-	-	50*	1000	250	28
AzF-25	I-29	1.0093	-	-	50*	1000	250	30
AzF-26	I-27/JF-5041	0.5/0.5	-	-	50*	1250	250	25
AzF-27	G22/2	1.0012	-	-	50*	1250	250	26
AzF-28	I-27/E-M-21853-8-3	0.5/0.5	-	-	50*	1250	250	28
AzF-29	CU-1986T	1.0056	-	-	50*	1250	250	24

*There was the same amount of Methanol added in addition to the feed amount displayed
^25mL of Methanol were also added
All reductions and reactions took place in a H_2 enviroment.

Table B. 4 Composition and Kinetic Dehydrogenation Results (Autoclave and Glass Reactors)

Run #	time hr	Wt. ratio Wliq/Wcat	% Dehydro Corrected	% Dimer + Polymer	% Decarbox.	Rate Const. hr^{-1}
HYR			25	3.8	0.1	
AzA3-3	1	280	27	4.5	0.14	9.42
AzA4-1*	1.7	240	37		0.18	
AzA4-2*	2.5		38		0.81	
AzA4-3	3.3		34	19.1	1.11	9.82
AzA9-1*	0.33	50	47		1.26	
AzA9-2*	0.67		50		0.94	
AzA9-3	1		49	8.4	0.94	15.25
AzA9-4	1.5		48	8.4	0.85	
AzA11-1*	44	100	38		0.39	
AzA11-2*	16		42		0.62	0.61
AzA11-3*	50.6		46		0.53	
AzA11-4	60		50	5	1.83	
AzA12-1	0.35	200	43	3.4	0.56	225.94
AzA12-2	0.33		61	5.5	0.74	
AzA12-3	0.33		60	5.5	1.17	318.22
AzA12-9	6		64	4.5	1.02	28.11
AzA12-10	post		63	7.3	0.9	
AzA14-1[1]	2	67	44	4.4		14.29
AzA14-2	0.5		54	5.2	0.93	59.11
AzA18-3	4.7	400	55	3.4	2.17	79.53
AzA18-4	1.25		60	3	2.17	163.54
AzA18-5	post		57	2.8	4.71	
AzA20-4	2.5	200	30	7.6	3.19	7.02
AzA21-2	0.5	380	40	5.8	4.31	235.74
AzA22-4*	2.5	200	28		5.89	4.09

(Table B.4 continued)

AzA23-2[2]	2.5	200	37	8	3.46	18.80
AzA23-3	1.8		48	8.7	4.39	37.09
AzA23-4	1		51	9.1	4.6	26.44
AzA23-5	post		49	9.3	7.64	
AzA24-1[3]	1.4	200	43	8.3	5.39	49.18
AzA24-2	1.1		55	8.9	3.22	98.01
AzA24-3	1.8		55	9	3.66	
AzA25-0	0	200				
AzA25-1	1.3		42	4.2	0.65	56.26
AzA25-2	0.7		50	4.2	0.69	82.30
AzA25-3	1.5		57	6.7	1.33	58.64
AzA25-4	1		57	7	3.55	
AzA25-5	post		58	6.3	0.83	
AzA26-4	2.8	200	29	7.4	2.48	4.94
AzA26-6	2.5		32	7.9	3.5	4.58
AzA26-7	post		32	6.1	4.1	
TAO			12	11.6	0	
AzA27-0	0	200				
AzA27-1	1		68	7.4	0.77	811.47
AzA27-2	2		68	7	1.06	
AzA27-3	1.8		67	8.3	0.91	
AzA27-4	1		68	7.9	1.4	
AzA27-5	post				1.46	
AzA28-0	0	200				
AzA28-1	1		65	7.4	2.2	371.23
AzA28-2	1		66	7.5	0.9	
AzA28-3	1.3		67	8.4	2.29	
AzA28-4	1		67	9.3	0.88	
AzA28-5	0.7		67	8	1.05	
AzA29-0	0	200				
AzA29-1	1		67		0.63	504.06

(Table B.4 continued)

AzA29-2	1				0.71
AzA29-3	2.3		67	8.2	1.03
AzA29-4	1				1.42

* Uncorrected for Polymer
[1]Run a continuation of run 11
[2]Run a continuation of run 20
[3]Run a continuation of run 22

Table B.5 Composition Results for Rosin Hydrogenations, mol%

Run #	stearyl	oleyl linoleyl	stearic	oleic	dihydro abietyl	abietyl	dihydro abietic	dehydro abietic	heavy
Az-6-4	0	2	0	18	0	0	0	1	0
Az-10-1	0	0.1	0.6	0.2	0	0	0	19	0.5
Az-13-1	0	0.1	0.9	0.5	0	0	0	19	1
Az-4-1	0	28	72	0	0	0	52	48	0
Az-6-1	0	8	40	52	8	0	59	17	0
Az-11-1	0	0.4	0.6	38	0	0	1.3	30	0.4
Az-12-1	0	0.1	0	17	0	0	0	31	0
Az-13-2	0	0	4.1	64	17	1.6	0	50	0.5
Az-14-3	0	0	0.2	38	15	1.7	0	38	1
Az-7-1	0	4	32	40	1		8	12	0
Az-1-2	2	9	63	26	4		51	26	4
Az-2-2	0	1	37	51	2		20	76	0
Az-10-3	0	0.1	0	15	0		0	26	0
Az-13-3	0	0	3	57	16	1.3	0.7	45	0.5
Az-11-2	0	0.3	1	6.4	0	0	0	20	0
Az-12-2	0	0.1	0.9	1.3	0	0	0	20	0.6
Az-13-4	0	0.1	1.7	9	2.6	0	0.1	21	0.5
Az-3-1	0	2	3	1	0	0	0	13	0
Az-1-3	0	3	52	41	22	0	43	16	0
Az-14-4	0	0	0.6	7.9	3.1	0.1	0.1	24	0.8
Az-5-4	0	9	0	7	0	0	3	0	0
Az-4-4	0	4	12	78	4	0	2	15	0
Az-7-2	0	7	1	20	0	0	0	3	0
Az-5-2	0	11	0	13	0	0	0	6	0
Az-4-2	0	1	85	14	12	0	67	17	0
Az-6-2	0	9	20	70	11	0	1	13	0

(Table B.5 continued)

Az-5-3	0	10	3	8	0	0	0	16	0
Az-4-3	0	7	50	25	2	0	48	16	0
Az-6-3	0	9	27	58	9	0	0	13	0
Az-3-1	0	3	8	2	0	0	0	11	2
Az-2-1	0	5	6	17	0	0	0	1	0
Az-11-3	0	1.3	1.4	7.1	0	0	0	22	0.2
Az-12-3	0	0.4	1.5	1.9	0	0	0	20	0.6
Az-8-2	0	15	1	0	0	0	0	3	0
Az-8-3	0	13	1	0	0	0	0	3	0
Az-3-4	0	3	3	5	0	0	0	13	0
Az-2-4	0	0	1	3	0	0	0	2	0
Az-10-2	0	0.4	6.5	6.4	0	0	0	21	0
Az-14-2	0	0	3.5	6.1	0.3	0	0.2	23	0.5
Az-7-3	0	6	17	5	0	0	2	19	0
Az-10-4	0	0	0.8	10	0	0	0	24	0
Az-14-1	0	0	3.2	17	0.8	0	0	23	0.9
Az-7-4	0	1	4	26	0	0	0	20	1
Az-11-4	0	0	0.3	12	0	0	0	22	0
Az-12-4	0	0.1	0.8	0.6	0	0	0	19	0.6
Az-3-4	0	2	0	0	0	0	0	8	0
Az-8-1	0	36	1	0	0	0	1	11	0
Az-8-4	0	0	0	0	0	0	2	0	0
Az-9-1	0	55	1	0	0	0	0	3	0
Az-9-2	0	65	1	0	0	0	0	2	0
Az-9-3	0	66	0	0	0	0	0	3	0
Az-9-4	0	70	1	0	0	0	2	3	0

Table B.6 Composition Results for Hydrogenations of Fatty Acid, mol%

GCMS Sample	Stearic	Stearyl	Oleic	Linoleic & Linolenic	Oleyl & Linoleyl	Pump Oil	Rosin Unkown	H_2 Selectivity
AzF-1F	23.3	1.3	64.1	5.6	0.0	0.0	5.7	-
AzF-1G	23.5	1.5	66.0	4.5	0.0	0.0	4.2	-
AzF-2A	10.0	1.8	71.5	11.8	0.9	0.0	4.1	-
AzF-2B	10.5	1.7	74.2	10.4	0.0	0.0	3.1	-

(Table B.6 continued)

AzF-3A	26.7	1.5	63.0	7.0	0.0	0.0	1.8	-
AzF-3B	27.4	1.2	62.4	8.0	0.0	0.0	0.9	-
AzF-4A	18.0	1.5	77.3	1.0	0.0	0.0	2.2	-
AzF-4B	17.6	1.7	76.3	2.2	0.0	0.0	2.2	-
AzF-5A	74.5	2.0	19.2	0.7	0.2	0.0	3.3	-
AzF-5B	73.3	2.0	20.3	0.0	0.3	0.0	4.1	-
AzF-6A	4.1	1.6	57.6	32.7	1.0	0.0	3.0	16.7
AzF-6B	4.1	1.5	59.2	34.4	0.0	0.0	0.8	11.8
AzF-7A	5.0	1.6	54.9	36.0	0.0	0.0	2.5	12.4
AzF-7B	5.2	1.7	55.0	36.0	0.0	0.0	2.0	12.5
AzF-8H	2.0	1.4	50.5	44.3	0.0	0.0	1.7	-0.1
AzF-8I	2.2	1.7	50.7	42.8	0.0	0.0	2.7	3.3
AzF-9A	6.4	1.5	53.3	37.7	0.0	0.0	1.1	11.2
AzF-9B	6.6	1.6	52.7	37.9	0.0	0.0	1.3	11.0
AzF-10A	4.8	1.8	58.0	33.4	0.3	0.3	1.3	15.5
AzF-10B	5.1	1.5	56.6	34.6	0.3	0.7	1.2	14.2
AzF-11A	2.9	1.7	57.0	36.4	0.2	0.2	1.7	9.7
AzF-11B	2.8	1.6	58.7	35.6	0.0	0.0	1.2	8.6
AzF-12A	3.0	1.3	53.2	40.8	0.0	0.1	1.6	4.0
AzF-12B	3.1	1.6	51.3	42.5	0.1	0.1	1.5	2.5
AzF-13A	2.1	1.5	51.2	43.4	0.0	0.0	1.7	0.8
AzF-13B	2.3	1.5	51.6	41.7	1.1	0.1	1.7	3.6
AzF-14-2C	2.4	1.7	52.0	40.9	2.4	0.3	0.3	5.8
AzF-14-2D	2.5	1.7	51.4	40.5	2.6	0.0	1.2	7.3
AzF-15-2B	36.3	1.2	48.9	12.5	0.4	0.0	0.7	67.2
AzF-15-2C	25.6	1.6	56.5	13.7	0.4	1.5	0.7	57.2
AzF-16-2A	6.5	1.4	56.8	27.1	5.2	2.6	0.4	28.7
AzF-16-2B	6.8	1.6	56.0	28.5	6.1	0.5	0.5	26.7
AzF-16-2C*	3.2	1.5	32.9	26.8	25.7	0.2	9.6	48.6
AzF-16-2D*	2.9	1.3	32.2	21.6	29.9	0.0	12.1	62.6
AzF-16-2B^	16.3	1.0	16.3	20.4	23.4	0.4	22.3	77.8
AzF-16-2C^	4.7	1.3	35.9	23.2	24.9	0.0	10.1	54.7
AzF-17-2A	8.3	2.0	52.5	35.9	0.3	0.0	0.9	16.2
AzF-17-2B	8.4	2.1	51.3	36.0	0.5	0.0	1.7	17.4
AzF-17-2B^	29.9	1.7	29.9	35.3	0.2	0.0	3.0	40.1
AzF-17-2C^	33.1	1.0	33.1	29.8	0.0	0.0	3.0	47.5
AzF-18-1A	9.8	2.3	64.4	15.6	0.5	0.3	7.1	46.0
AzF-18-1B	8.0	2.4	63.3	16.1	0.4	0.2	9.6	46.2
AzF-19-1D	7.3	2.2	49.5	30.3	1.9	1.7	7.1	29.8

(Table B.6 continued)

AzF-19-1E	6.2	2.2	50.0	35.6	1.0	1.4	3.6	18.2
AzF-20-1A	17.3	1.9	55.8	20.5	0.6	0.2	3.6	44.3
AzF-20-1B	19.1	1.9	53.1	21.3	0.6	0.4	3.6	45.2
AzF-21-1A	6.8	2.1	55.2	31.0	1.7	0.2	3.1	22.2
AzF-21-1G	8.8	2.1	50.7	33.6	1.4	0.0	3.4	21.5
AzF-22-1A	78.5	1.2	19.8	0.0	0.0	0.0	0.5	121.8
AzF-22-1B	78.4	1.1	20.0	0.0	0.0	0.0	0.5	121.4
AzF-23-1E	1.6	33.8	52.8	9.5	0.7	0.0	1.5	100.0
AzF-23-1F	33.8	2.0	52.0	9.2	1.1	0.0	1.8	70.9
AzF-23-2B*	2.8	18.3	64.4	9.7	0.0	2.6	2.3	73.6
AzF-23-2C*	2.3	18.5	66.0	7.8	0.7	2.0	2.6	75.9
AzF-24-1C	10.1	2.0	69.1	15.9	0.4	0.0	2.5	40.0
AzF-24-2B*	8.9	2.1	64.4	14.4	2.0	0.6	7.6	47.6
AzF-24-2*C	8.1	2.1	60.9	18.8	2.3	0.2	7.6	41.1
AzF-24-3A	7.7	2.0	53.4	33.9	0.4	0.0	2.7	18.9
AzF-24-3B	6.2	2.2	53.9	30.3	0.6	0.2	6.7	26.1
AzF-24-4A*	2.8	2.0	55.6	34.5	0.6	0.0	4.5	15.8
AzF-24-4B*	5.7	1.8	44.6	37.0	3.0	0.0	7.8	19.3
AzF-25-1A	10.2	2.2	54.7	30.1	0.3	0.3	2.3	25.1
AzF-25-1B	12.5	2.1	50.8	30.1	0.9	0.1	3.5	29.8
AzF-25-2A*	4.6	2.0	46.3	29.2	6.0	2.1	9.8	35.4
AzF-25-2B*	4.9	1.9	45.0	33.7	7.3	0.0	7.2	27.8
AzF-25-3C	2.8	1.8	49.2	38.6	0.8	2.3	4.5	13.3
AzF-25-4A*	1.3	2.1	42.8	43.7	1.8	0.1	8.0	8.1
AzF-25-4B*	2.0	2.0	42.5	40.4	5.7	0.0	7.5	17.0
AzF-26-1H	12.7	2.4	61.4	18.7	0.1	0.1	4.6	42.1
AzF-26-1I	12.8	2.5	61.7	18.5	0.1	0.1	4.3	42.6
AzF-26-2E*	14.2	0.0	79.0	6.7	0.0	0.0	0.0	47.4
AzF-26-2F*	15.4	0.0	76.8	7.8	0.0	0.0	0.0	47.4
AzF-26-3H	3.6	2.4	50.8	39.2	0.4	0.6	3.0	10.8
AzF-26-3I	3.5	3.1	50.2	40.6	0.0	0.3	2.3	8.7
AzF-27-1A	10.4	3.3	55.1	26.6	2.2	0.0	2.5	32.3
AzF-27-1B	11.5	2.1	56.7	25.1	1.8	0.2	2.5	32.1
AzF-27-2B*	8.9	1.5	58.3	26.4	1.8	0.0	3.1	29.3
AzF-27-2D*	8.5	1.3	53.2	32.1	1.8	0.0	3.2	21.6
AzF-28-1A	6.5	2.9	56.3	31.4	1.2	0.0	1.7	20.1
AzF-28-1B	6.3	2.7	56.0	31.8	0.8	0.0	2.4	20.2
AzF-28-2A*	3.7	2.4	51.0	32.6	0.4	0.0	9.9	24.3
AzF-28-2B*	3.4	3.7	50.6	35.1	0.3	0.0	6.9	21.3

(Table B.6 continued)

AzF-28-3A	3.2	2.5	47.1	42.7	0.9	0.0	3.7	5.8
AzF-28-3B	3.1	2.6	47.0	44.1	0.6	0.2	2.5	1.7
AzF-29-1A	16.3	2.5	52.2	25.6	0.6	0.3	2.7	36.2
AzF-29-1C	15.7	2.5	51.3	27.0	0.5	0.4	2.6	34.3
AzF-29-2A	10.4	0.0	56.8	21.1	2.2	0.9	8.6	40.0
AzF-29-2B	9.1	1.1	58.9	19.2	1.3	0.6	9.7	42.9
AzF-29-3A	7.1	2.6	48.0	40.3	0.1	0.2	1.7	6.6
AzF-29-3B	6.8	2.5	49.3	39.2	0.1	0.0	2.1	9.7

* Esterified Methanol Phase ^ Unesterified Methanol Phase

VITA

Edward O'Brien was born in St. Louis, Missouri, to Frank and Jean O'Brien in August 1986. He attended the University of Dallas and graduated in May 2009 with a Bachelors of Science in chemistry. The following summer he began the master's program at Louisiana State University, and this thesis will complete his requirements to graduate with a Master of Science in Chemical Engineering.